**Monolithic Solid Oxide Fuel Cell Technology Advancement
for Coal-Based Power Generation**

**Final Report
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FOREWORD

This report was prepared by AlliedSignal Aerospace Systems & Equipment (ASE) in partial fulfillment of the statement of work (SOW) for Contract DE-AC21-89MC26006. Item 1 of Section C, "Deliverables," references the "Reporting Requirements Checklist" (Part III, Section J, Attachment B of the subject contract). This checklist calls for the submittal of the final technical report.

This final technical report covers the period of performance of the subject contract: September 27, 1989 through December 30, 1993. It describes the contractual effort performed by ASE, Argonne National Laboratory (ANL), Combustion Engineering (CE), and the University of Oklahoma for the U.S. Department of Energy, Morgantown Energy Technology Center (METC).

The objective of the project is to advance materials and fabrication methodologies to develop a monolithic solid oxide fuel cell (MSOFC) system meeting performance, life, and cost goals for coal-based power generation. The program focuses on materials research and development, fabrication process development, cell/stack performance testing and characterization, cost and system analysis, and quality development.

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1. BACKGROUND ON MONOLITHIC SOLID OXIDE FUEL CELLS

The monolithic solid oxide fuel cell (MSOFC) is a recent design concept in fuel cell technology. The MSOFC is made up of all solid components, permitting fabrication into unique shapes unachievable in fuel cell systems having liquid electrolytes. The MSOFC design places the thin ceramic components of the fuel cell in a lightweight, compact structure of very small cells. The monolithic design eliminates inactive structural support, increases active surface area, and lowers voltage losses caused by internal resistance. This results in a MSOFC with high efficiency, excellent performance, and power per unit mass or volume unequaled in any other solid oxide fuel cell configuration.

1.1 DESIGN CONCEPT

In a MSOFC, fuel and oxidant produce a dc current by combining electrochemically across the solid oxide electrolyte at an operating temperature of 1000°C. Oxygen in the oxidant fed to the cathode accepts electrons from the external circuit to form oxide ions that are then conducted through the dense electrolyte to the anode. At the anode, oxide ions combine with hydrogen in the fuel to form water, liberating electrons as shown in Figure 1-1. Cells of the MSOFC are connected by an interconnect to build voltage. The interconnect carries electrons from the anode of one cell to the cathode of the next in electrical series.

Figure 1-1. Solid Oxide Fuel Cell Chemistry

There are two versions of the MSOFC, coflow and crossflow. In the coflow version, the monolithic fuel cell consists of a honeycomb-like array of adjacent fuel and oxidant channels that resemble corrugated paperboard (Figure 1-2). Oxidant channels are lined with a porous cathode, and fuel channels are lined with a porous anode. A gastight layer of electrolyte is located between the anode and cathode. An interconnect, which is also gastight, connects the cells in electrical series.

Figure 1-2. Coflow Monolithic Solid Oxide Fuel Cell

The typical thickness of the layers is 25 to 100 μm , and the distance from cell to cell is 1 to 2 mm. As shown in Figure 1-2, the MSOFC is made of two types of laminated structures, each composed of three ceramics—anode/electrolyte/cathode and anode/interconnect/cathode. The laminated structure containing the electrolyte is appropriately corrugated. The corrugations form the gas seals at the edges of the monolithic structure (which is extremely important because the gas seal has been a stumbling block in solid oxide fuel cell planar design).

In the crossflow version, the fuel and oxidant channels are formed by corrugated anode and cathode layers and are oriented at right angles to each other (Figure 1-3). The anode/electrolyte/cathode and anode/interconnect/cathode composites are flat and stacked alternately between the corrugated anode and cathode layers. The crossflow version results in the power density being reduced by a factor of about 2, compared with that of the coflow version; however, the crossflow version offers a simpler means of ducting gases in and out of the monolithic fuel cell.

1.2 DESIGN FEATURES

Small cells of lightweight self-supporting ceramics are the key to the MSOFC potential. The small size of individual cells in the monolithic structure increases the active surface area. For example, a coflow MSOFC with channels about 1 mm in diameter has a ratio of active surface area to volume of about $9.4 \text{ cm}^2/\text{cm}^3$ (Figure 1-4). This is about seven times the ratio for tubular solid oxide fuel cells of 1 cm in diameter.

More importantly, the small cell size in the MSOFC reduces voltage losses due to internal electrical resistance. Because current is carried in-plane by the electrodes in both conventional and monolithic designs, a decrease in the cell size decreases the

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Figure 1-3. Crossflow Monolithic Solid Oxide Fuel Cell

Figure 1-4. Monolithic Configuration, Providing a Maximum Active Surface Area per Unit of Volume

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internal electrical resistance. In MSOFC's, the major source of internal voltage loss is the resistance that electrons encounter in the cell ceramic components. Inside the operating fuel cell, an oxidation reaction (the electrochemical reaction of hydrogen fuel) releases electrons on the anode side of the barrier that separates oxygen channels from fuel channels. Flowing along the anode, electrons travel around the fuel-channel wall and across the interconnection to the cathode of the adjoining oxygen channel (Figure 1-2).

The electrons then flow along the cathode around the oxygen channel to the cathode/electrolyte interface, where they are consumed in a reaction (with oxygen) that produces an oxide ion. The oxide ion is transported through the plane of the electrolyte, reacts with hydrogen on the fuel side of the electrolyte to produce electrons, and the process continues. In this way, the electron current traverses the multicell monolithic structure. Because individual cells in the monolithic fuel cell are small, electron/ion paths are short and resistive losses are low. The lower resistance of the monolithic fuel cell improves cell efficiency by about 10 percent. As a result of lower internal resistance, the MSOFC's can be operated at higher current densities than conventional fuel cells while achieving the same output voltage.

The power density for the MSOFC is higher than that of conventional solid oxide fuel cells and other electrical power-generating technologies. The high power density results from the higher surface area, higher current density, and lower weight. The lower weight in the monolithic design is primarily the result of eliminating inert supports, which is possible because the thin ceramic layers are self-supporting. Because of the shorter current paths involved in the monolithic design, electrodes can be thinner, which reduces weight further.

Because the monolithic design employs thin electrodes, diffusion losses are minimized. The cell voltage is determined by the pressures of the reactants and products at the electrode/electrolyte interface. Thus, any reduction in the pressure at the reaction site represents a loss in voltage, and therefore efficiency. A loss in voltage due to reduced pressure is given by

$$[RT/nf] \ln (P_{\text{eff}}/P_{\text{gas}})$$

where P_{eff} is the pressure at the interface

P_{gas} is the pressure of the bulk gas steam

P_{eff} is dependent on the diffusion of reactants and products through the electrodes. In tubular designs, the thick support tube (30 percent porosity) and thick electrodes represent large diffusional barriers. The monolithic design minimizes diffusion losses by eliminating the thick support tube and employing thin electrodes.

In addition to gas diffusion limitations, a potential barrier exists to charge transport across phase boundaries between the electrodes and the electrolyte. This is associated with the electrode reactions. The voltage loss due to this barrier is the activation potential. At the operating temperature of the MSOFC, reaction rates are very

rapid, so it is not necessary to provide a very thick electrode to ensure sufficient active surface area.

Practical cell operation is always strongly exothermic. Cooling is required in order to maintain a desired cell operating temperature. The MSOFC can be cooled by providing excess oxidant beyond that required by the cell reaction. The temperature rise of this stream will carry off heat. The MSOFC can also be cooled by heat-absorbing reactions within the cell. If the fuel is a relatively complex molecule, it can be broken down or reformed in the cell. These reactions are endothermic and can contribute substantially to cell cooling. Examples are the steam reforming of methane and other hydrocarbons such as those found in natural gas, coal gas, and those produced in the decomposition of methanol.

Fabrication of the MSOFC requires incorporation of four thin cell components into the monolithic structure. The MSOFC is fabricated by forming thin ceramic components as green (unfired) layers, incorporating them into the monolithic structure, and cofiring the structure at elevated temperatures to form the required sintered body. Since the fabrication of the fuel cell requires only a single high-temperature processing step, the MSOFC has potential for low-cost manufacturing.

Table 1-1 summarizes the key features and the benefits offered by the MSOFC design.

TABLE 1-1	
FEATURES AND BENEFITS OF MONOLITHIC DESIGN	
Feature	Benefit
Small cell size	<ul style="list-style-type: none">● Increased active surface area● Low internal resistance● Improved efficiency
Corrugated structure	<ul style="list-style-type: none">● No high-temperature seals● Robust structure
Self-supporting structure	<ul style="list-style-type: none">● Lightweight● Compactness● High power and energy densities
Single high-temperature processing step	<ul style="list-style-type: none">● Potential low-cost manufacturing

2. EXECUTIVE SUMMARY

This project has successfully advanced the technology for monolithic solid oxide fuel cells (MSOFC's) for coal-based power generation. Major technology advancements include:

- Advancing the state of the art of tape-calendering processing technology. These advances have permitted the scaled fabrication of ultra-thin electrolytes on an anode substrate, leading to a three-fold improvement in cell performance at 1000°C.
- Developing stack materials formulations and designs that achieve a sufficiently close thermal expansion match that no stack damage is observed even with repeated thermal cycling in air.
- Developing electrically conducting bonding technology that shows excellent structural robustness even with repeated thermal cycling in air.
- Developing sealants that form good mechanical seals for forming manifold structures.

A stack testing facility has been designed and built to accommodate high-power MSOFC stacks. The facility is capable of automatically providing fuel and oxidant flows up to 100 standard l/min, measuring up to 100 amp of current and 1 kw of power, while precisely establishing the stack operating temperature.

Several comprehensive models have been developed.

A fuel cell performance model called FCELL, originally developed at ANL, was upgraded to include important heat transfer effects and better establish fuel cell constituents in the oxidant and fuel stream.

An ANSYS-based model has been developed to analyze structural stresses in multicell stacks that have been induced during the cool-down portion of the thermal processing cycle and during fuel cell operation. This model has led to greatly improved structural designs.

A model has been developed to analyze the electrical resistance of various stack configurations.

Moreover, various mechanical and chemical compatibility properties of fuel cell components have been measured. These measurements have formed the data base for the structural assessments. They show that the baseline Ca-, Co-doped interconnect expands and weakens in hydrogen fuel. This factor and the failure to develop adequate sealant technology were the principal factors causing performance shortfalls in large stacks. Small (1-in. footprint) two-cell stacks were fabricated which achieved good performance (average area-specific-resistance (ASR) of 1.0 ohm-cm² per cell). However, larger stacks exhibited stress-induced structural defects sufficient to cause poor performance.

The various technical tasks associated with this effort are reviewed below.

2.1 MATERIALS RESEARCH AND DEVELOPMENT

The materials research and development activities culminated with a set of monolithic solid oxide fuel cell (MSOFC) stack materials which were sufficiently compatible so that the stack could be thermally cycled in air with no apparent performance-compromising defects. The key for this success was to design the fuel cell with thin-film electrolyte and thin-film cathode cells, and developing stack designs making the anode and interconnect the principal structural elements. A very close match of the thermal expansion characteristics of the anode and interconnect was achieved, reducing stack stresses to acceptable levels.

However, the baseline calcium-, cobalt-doped lanthanum chromite interconnect was found to expand and weaken in the hydrogen fuel environment, creating significant structural damage to the large-scale stacks, and seriously affecting stack performance. Alternative lanthanum chromite interconnect materials show better stability in hydrogen, but have a poor thermal expansion match to the baseline anode and interconnect materials.

Additionally, attempts to cofire the lanthanum chromite interconnect in contact with the anode and cathode materials have met with only moderate success.

Three approaches were explored for obtaining a dense interconnect as follows:

- (a) Fabricate a two-material cell that consists of only electrolyte and interconnect materials. These materials are formed into five layers symmetrically configured around the zirconia electrolyte. The outer two layers comprise zirconia/lanthanum chromite mixtures to improve bonding. The layer closest to the electrolyte called the bond coat contains greater weight percent zirconia than lanthanum chromite, whereas the opposite is true for the outer layer. A summary of the results of a series of tests is presented in Table 2-1. The best performance achieved to date (1.91-ohm centimeter squared) is not adequate for fuel cell stack criteria.
- (b) Fabricate a three- or four-material cell with a sintering aid that does not melt until after the onset of densification in the electrodes. Early tests with calcium- and cobalt-doped lanthanum chromite showed the formation of a liquid phase at 1050°C, clearly before the onset of electrode sintering, and densification of the interconnect was not achieved.

By replacing calcium with strontium in the lanthanum chromite formulation the liquid formation temperature was increased to 1250°C. Trilayer tapes of anode and interconnect (AIA) and cathode and interconnect (CIC) were fired at 1500°C in air. Interconnects densified well in the AIA assemblies and a dense layer formed in the CIC, but the dense layer was thin and interaction between the interconnect and cathode was still evident.

TABLE 2-1

AREA-SPECIFIC RESISTANCE (OHM-CM²) OF IEI COMPOSITES AT 1000°C

Sample	Air Atmosphere		H ₂ /H ₂ O Atmosphere		Air and H ₂ /H ₂ O		Total
	Interfacial	Bulk	Interfacial	Bulk	Interfacial	Bulk	
IEI	0.184	0.484	2.91	1.10	3.58	0.801	4.38
IEI-8	0.109	1.17	1.40	2.79	1.63	2.11	3.74
IEI-15	0.124	0.475	0.790	1.16	1.01	0.905	1.91
IEI-16	0.148	0.356	1.48	1.58	1.62	1.17	2.51
IEI-18	0.149	0.415	1.04	1.32	1.35	0.940	2.29
IEI-19	0.100	0.915	0.678	1.18	(0.780)	(1.05)	(1.83)

() = Calculated from single atmosphere results.

Compositions:

IEI: doped LaCrO₃, YSZ, doped LaCrO₃.

IEI-8: 35 wt% YSZ/65 wt% doped LaCrO₃, YSZ, 35 wt% YSZ/65 wt% doped LaCrO₃.

IEI-15,18,19: 35 wt% YSZ/65 wt% doped LaCrO₃, 80 wt% YSZ/20 wt% doped LaCrO₃, YSZ, 80 wt% YSZ/20 wt% doped LaCrO₃, 35 wt% YSZ/65 wt% doped LaCrO₃.

IEI-16: 35 wt% YSZ/65 wt% doped LaCrO₃, 65 wt% YSZ/35 wt% LaCrO₃, YSZ, 65 wt% YSZ/35 wt% LaCrO₃, 35 wt% YSZ/65 wt% doped LaCrO₃.

- (c) Form the anode-interconnect-cathode trilayer with ultra-thin electrode layers (no thicker than 12 microns) to volumetrically limit sintering aid migration. Although densification of interconnects in AIC trilayers was achieved, when Al, Cl, and AIC assemblies were cofired with electrode corrugates significant fracturing and warpage of the assemblies occurred, indicating significant mismatch of firing shrinkage and component coefficient of thermal expansion. Additionally, near the bond region between the bilayer and the electrode corrugates significant porosity occurs (Figure 2-1).

An electrochemical model for the SOFC initially developed by Argonne National Laboratory was transferred to the University of Oklahoma for further development. This model does not predict well the polarization curve under some conditions of interest. In particular, the second derivative of the polarization curve for operation of an SOFC in hydrogen/oxygen at low current densities is predicted negative by the model, whereas experimental studies show it to be positive. Parametric studies of the model parameters have failed to explain the lack of correspondence between the model and experimental measurements. This failure suggests that the reaction mechanisms may not be accurate or complete. In particular, a second, parallel hydrogen oxidation mechanism may be operating at the anode surface. This second mechanism involves hydrogen adsorption at an adsorbed water site, followed by hydrogen ion diffusion to the electrolyte.

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Figure 2-1. Optical Micrograph of a Polished Cross Section of A/I Bonded to an Anode Corrugation Showing Porosity (Gray Area) by Bond Region

To evaluate the effects of long-term operation on the cathode the interfacial resistance of symmetrical cathode/electrolyte/cathode composites was measured in long-duration tests at 1000°, 1100°, and 1200°C (see Figure 2-2). Because the porosity decreases continuously with time and most of the manganese migration occurs in the first part of the test, the increase in the interfacial resistance with time can be attributed to the densification of the cathode due to sintering. Because sintering is basically a diffusional mechanism, the density changes approximately proportionally to the square root of time. Using data from tests similar to that described above, it was found that at 1000°C, 23,000 hr of operation are required before a significant change in the interfacial resistance (0.1 ohm-centimeters squared) occurs.

It was found, as expected, that the presence of sulfur in the fuel caused a significant degradation in the performance of the fuel cell (see Figure 2-3). However, as shown, periodic removal of the sulfur causes the fuel cell to rapidly recover its original performance. A small effort was undertaken to evaluate the addition of specific additives to the anode to reduce its sensitivity to sulfur. These additives proved to increase the resistance of the anode to sulfur contamination (see Figure 2-4).

The density, strength, and elastic modulus of cathode, anode, and electrolyte specimens were measured at ANL. For these studies approximately 15 specimens of each component were fired at a specified temperature, progressing from 900° to 1350°C. The specimens were formed into discs with a diameter of approximately 1 in.,

Figure 2-2. C/CE/E/CE/C Composite Area Specific Interfacial Resistance vs Time in Air

Figure 2-3. Performance of Anode with Sulfur

Figure 2-4. New Anode Formulation Shows Improved Sulfur Tolerance

and were approximately 10 to 14 mil thick. The results of the evaluations are shown in Tables 2-2 through 2-4.

TABLE 2-2			
MEASURED PROPERTIES OF INTERMEDIATE (CATHODE) SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.35 ±0.06	8.5 ±0.38	9.61 ±1.85
1000°C/0.0 hr	3.39 ±0.05	12.8 ±0.83	14.16 ±3.63
1100°C/0.0 hr	3.42 ±0.05	18.6 ±0.73	25.50 ±3.24
1200°C/0.0 hr	3.68 ±0.14	29.3 ±1.20	38.40 ±7.00
1300°C/0.0 hr	4.45 ±0.12	83.1 ±7.20	49.30 ±11.60
1350°C/0.0 hr	4.85 ±0.14	105.1 ±8.00	66.30 ±7.70
1350°C/0.5 hr	5.01 ±0.20	122.7 ±10.20	63.30 ±7.90

TABLE 2-3			
MEASURED PROPERTIES OF ANODE SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.24 ±0.01	14.9 ±1.81	7.51 ±0.92
1000°C/0.0 hr	3.37 ±0.17	16.7 ±0.70	9.35 ±1.80
1100°C/0.0 hr	3.43 ±0.14	18.6 ±0.73	20.65 ±3.10
1200°C/0.0 hr	3.76 ±0.01	30.9 ±2.12	35.60 ±5.89
1300°C/0.0 hr	4.68 ±0.38	59.7 ±9.94	64.74 ±12.10
1350°C/0.0 hr	5.52 ±0.23	134.0 ±9.30	76.01 ±15.80
1350°C/0.5 hr	5.68 ±0.33	138.4 ±19.80	101.30 ±14.51

TABLE 2-4			
MEASURED PROPERTIES OF ELECTROLYTE SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.13 ± 0.04	16.35 ± 0.91	8.58 ± 1.22
1000°C/0.0 hr	3.13 ± 0.09	25.44 ± 2.08	15.41 ± 3.92
1100°C/0.0 hr	3.14 ± 0.38	53.11 ± 4.60	29.48 ± 10.13
1200°C/0.0 hr	3.55 ± 0.12	52.46 ± 4.13	63.80 ± 20.20
1300°C/0.0 hr	4.81 ± 0.12	149.13 ± 13.50	105.40 ± 33.31
1350°C/0.0 hr	5.03 ± 0.14	185.31 ± 8.30	126.70 ± 33.24
1350°C/0.5 hr	5.51 ± 0.40	212.35 ± 6.20	158.30 ± 40.12

Several different bonding formulations were developed and tested at various levels of cell integration. Several types of single-cell stacks were constructed, differing in the layer used for cover plates and/or the bonding formulations. The purpose of this effort was to identify bond formulations for building multicell stacks and assessing the effect the different cover plates and bond formulations would have on performance. Table 2-5 summarizes the results obtained on stacks constructed for this effort. As seen from Table 2-5, stacks with an interconnect plate substituting for an anode cover had poor CE bonds and a tendency to delaminate during application of the current collector. This indicates a weak bond and poor thermal cyclability. From these results and performance test results, no further work on the use of the interconnect as a cover plate along with the CE cover plate was pursued.

A polished cross section of a bonded two-cell stack is shown in Figure 2-5. It is a sister stack to one that performed with an area specific resistance of less than 2.5-ohm-centimeter squared. Further improvement in bonding was noted when the anode-interconnect bond comprised anode material only.

Several attempts were made to modify ANL's "K" glass to form a seal between the manifold and stack and to seal the fuel and oxidant passages from the oxidant and fuel, respectively. Although the "K" glass formed good seals between electrolyte materials, attempts to bond the other cell components to one another or to the electrolyte were not successful. It appears that the principal difficulty is that the glass promotes physical deformation at the interfaces due to chemical changes and concomitant stress-induced mechanical strain.

2.2 FABRICATION

The ultimate objective of monolithic solid oxide fuel cell (MSOFC) development is to produce a product that can be manufactured in a single thermal processing cycle

TABLE 2-5			
EFFECTS OF DIFFERENT COVER PLATES AND BOND FORMULATIONS			
Stack Construction	Anode Bond Formulation	CE Bond Formulation	Result
A-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds; tested
	A/I (75/25)	CE/I (25/75)	Poor bonding
	A/I (50/50)	CE/I (50/50)	Good bonding
A-sc mod-I	A/I (100/0)	CE/I (50/50)	Good bonds; tested
I-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds: CE plate delaminated during test preparation.
I-sc mod-I	A/I (100/0)	CE/I (50/50)	Poor CE/I bond; CE plate delaminated during test preparation.
	A/I (75/25)	CE/I (25/75)	Poor CE/I bond
	A/I (50/50)	CE/I (25/75)	Poor CE/I bond; CE plate delaminated during test preparation.
Note: sc mod means single-cell module			

and configured such that the anode/electrolyte/cathode (A/E/C) trilayer is corrugated and manifolded in a coflow configuration. The former attribute reduces the costs of stack processing, whereas the latter increases the achievable power density of the MSOFC, reducing material costs. However, the technical challenges associated with developing the associated technology are significant. Because of the anticipated difficulties in manifolding a corrugated coflow MSOFC, a crossflow approach with a planar cell and corrugated electrode configuration was selected as the baseline construction at program inception.

The materials issues encountered are discussed in Section 3. Early in the project it was recognized that developing an interconnect that could be fired simultaneously with the electrodes would be a difficult and time-consuming task. Although a significant effort was undertaken to develop a "cofired" interconnect, an alternative approach was undertaken to cofire single cells with electrode corrugates and bond them with sintered interconnects (see Figure 2-6). This approach proved successful at small scale, but at footprints larger than approximately 2 in. by 2 in. the yield of the cofired assemblies was very low. Subsequently, an approach involving the bonding of sintered cells, electrode bars, and interconnect plates was adopted, and this was the baseline for scaled fabrication (see Figure 2-7).

During the course of this project AlliedSignal's thin-film electrolyte cell technology was developed. This process involves sequentially rolling bilayer tapes of anode and electrolyte in such a manner that the electrolyte layer is ultra-thin (see Figure 2-8). The

F-65883

Figure 2-5. Polished Cross Section of Bonded Two-Cell Stack (EE344-01)

Figure 2-6. Two-Step MSOFC Assembly

IG-19461A

Figure 2-7. Plate-and-Bar Construction of MSOFC's

Figure 2-8. Schematic Diagram of Fabrication Process for Thin-Electrolyte Cells

bilayer is then cofired, a cathode slurry is applied to the bilayer, and the cell is fired. In this manner uniform electrolyte layers as thin as 1 micrometer can be formed (see Figure 2-9). This construction technique leads to cells which exhibit the best

F-68138

Figure 2-9. Fracture Surface of Sintered Electrolyte/Anode Bilayer

performance of all known fuel cells. At 1000°C, a power density of 1 w per square centimeter has been achieved. It was demonstrated that the cells fabricated in this manner can be scaled to an area of 500 square centimeters with high fabrication yield. These cells were used in the plate and bar stack construction.

The task was to culminate in the fabrication of a 100-w stack. Although several manifolded stacks were built (see Figure 2-10) that had the potential (based on single-cell performance and stack resistivity analysis) to achieve 100 w, the tests were not successful.

However, with a combination of good component thermal expansion matching and stack designs, which minimized component stresses, manifolded stacks were fabricated that could be thermally cycled in air with no evidence of performance-compromising damage. Due to difficulties with hydrogen compatibility of the lanthanum chromite interconnect material and the lack of a suitable sealant, significant stack defects occurred when hydrogen was introduced to the fuel cell. These defects were sufficient to cause the performance shortfalls exhibited by the stacks.

A review of materials suppliers was undertaken to establish a new baseline for material costs for the updated cost studies and to evaluate potential suppliers.

The evaluation concluded that commercial raw material suppliers exist who can be fully compliant with the anticipated material requirements in the foreseeable future to

F-66389

Figure 2-10. Photograph of Three-Cell Stack After Firing

support the commercial manufacture of MSOFC's. Several of the identified raw materials that meet these anticipated requirements are currently available. Changes to the raw materials identified in this evaluation will most assuredly occur as the development process evolves and improvements are made. These raw material changes could therefore affect the identification of material suppliers who are fully compliant with the anticipated material requirements.

This study revealed an estimated raw material cost to manufacture the MSOFC that falls nearly midway between the current and economic costs used in the previous manufacturing cost study. This cost level should not affect the financial viability of commercially manufacturing the MSOFC. Evaluations of lower purity materials should be performed that could substantially reduce the raw material cost of MSOFC manufacture.

2.3 TESTING ON COAL GAS

Tests of the thin-film electrolyte cells have shown power density exceeding 900 mw per square centimeter at 1000°C and approximately 550 mw per square centimeter on hydrogen-air (see Figure 2-11). However, for the reasons stated previously, no successful tests were completed with the large-scale stacks incorporating the thin-film electrolyte technology. However, a number of successful tests was completed with small-scale (1-in. by 1-in. footprint) stacks. These stacks incorporated cells which were approximately 300 micrometers thick with thickness ratios for the anode/

Figure 2-11. Thin-Electrolyte Cell Performance

electrolyte/cathode at 2/1/1. The stacks were made by bonding single-cell modules to ceramic interconnect plates. Results of the testing are shown in Figure 2-12.

A performance test of a two-cell stack demonstrated an average per-cell ASR of 1.0-ohm-centimeter squared. Another two-cell stack was tested with an applied load of 200 ma for 600 hr. The ASR of the stack initially measured 2.5-ohm-centimeter squared. After 600 hr of operation, the ASR of the stack had improved to 2.15-ohm-centimeter squared. A four-cell stack producing more than 1 watt was tested. The average per-cell ASR was approximately 2.5-ohm centimeter-squared. A two-cell stack was tested on simulated coal gas (67 percent hydrogen, 22 percent carbon monoxide, 11 percent water) and air at 800°C, 900°C, 1000°C, and 1050°C. The results of the tests are displayed in Figure 2-13. A two-cell stack was tested in humidified hydrogen and air at 800°, 900°, 1000°, and 1050°C. The results of these tests are shown in Figure 2-14.

Posttest analyses of tested stacks showed continual improvement in the second-step bond of the stacks, particularly the anode-to-interconnect bond. All the bonds appeared to show much better contact, providing sufficient electrical connection between cells for low-resistance current flow within the stack. A dramatic reduction in delamination at the bonding sites was observed with use of the glass manifold sealant technology.

— TWO-CELL STACK
 - - - FOUR-CELL STACK

IG-11877
 8-19-92

Figure 2-12. Performance of Multicell Stacks

IG-14281

Figure 2-13. Two-Cell Stack Performance with 67% H₂ + 22% CO + 11% H₂O/Air

IG-14282

Figure 2-14. Two-Cell Stack Performance with 97% H₂ + 3% H₂O/Air

2.4 PERFORMANCE AND COST ANALYSIS

A mathematical model of the MSOFC called FCELL has been completed. The model simulates the electrochemical, electrical, thermodynamic, and chemical equilibrium processes occurring in the cell. A single cell within the MSOFC stack is modeled. This cell is assumed to be sufficiently deep within the stack so that end effects may be neglected. The horizontal plane of the cell is divided into a two-dimensional grid of rectangular area or elements. Each element has a single, centrally located node. The elements are sufficiently small so that the nodal values of temperature, pressure, concentration, etc. can be used over the entire element for the calculation of local current densities and heat fluxes. The mass balance, energy balance, and expressions for the electrochemical and electrical phenomena are set up and solved for each element.

The inputs to the program include the geometry of the fuel cell, the cell operating voltage, and inlet fuel and oxidant temperatures, pressures, flow rates, and compositions. The model can operate with any fuel that contains any or all of the following constituents: hydrogen, water, simulated diesel fuel, carbon monoxide, carbon dioxide, methane, oxygen, or nitrogen. Air or pure oxygen can be used as the oxidant. If desired, the program can operate in a mode in which the user specifies the cell current, fuel utilization, or maximum desired cell temperature in place of the cell voltage or one of the inlet flow rates. In this mode of operation, the program uses an additional iteration loop to determine the cell performance based on the input values. The program outputs include the temperature, composition, Nernst potential, and current at each node. Also, a number of performance parameters are calculated such as the fuel and oxidant utilization, total cell power, fuel efficiency, and average temperatures.

Market assessments have been made for solid oxide fuel cells distributed and baseload power generation in the United States. Synopses of the data are displayed in Tables 2-6 and 2-7.

The stack model was coupled with a system simulation model capable of modeling mass and energy balances in chemical process equipment to perform system configuration studies. These studies projected very high efficiencies for a 2-Mw natural gas-fired plant based on MSOFC technology. A process flow diagram for a high efficiency SOFC plant is shown in Figure 2-15. Table 2-8 presents detailed flow stream data.

Additionally, the stack manufacturing costs previously developed under DOE/METC Contract DE-AC21-88MC25166, "Yttria-stabilized Zirconia Solid Oxide Electrolyte Fuel Cells-Monolithic Solid Oxide Fuel Cells," were updated with information gained from material suppliers and to reflect the change in the MSOFC technology base associated with the incorporation of thin-film electrolytes. The material costs, as estimated by materials suppliers, are presented in Table 2-9. The updated annual operating costs for a plant producing 200 Mw (equivalent) of MSOFC stacks per year are shown in Table 2-10.

TABLE 2-6

**ANNUAL U.S. DISTRIBUTED GENERATION SOFC
MW GROWTH AND 1994 \$ VALUE**

Year	DG FC, Mw	SOFC Penetration, percent	SOFC Penetration, Mw	\$, kW Installed	Total \$, MM Installed	\$, MM Stack
2001	11	0	0			
2002	32	0	0			
2003	64	5	3	1500	5	2
2004	134	15	20	1250	25	13
2005	322	30	96	1000	96	48
2006	563	45	253	1000	253	127
2007	750	55	413	1000	413	206
2008	938	60	563	1000	563	281
2009	1126	65	732	1000	732	366
2010	1313	70	919	1000	919	460
2011	1540	70	1078	1000	1078	539
2012	1540	70	1078	1000	1078	539
2013	1540	70	1078	1000	1078	539
2014	1540	70	1078	1000	1078	539
2015	1540	70	1078	1000	1078	539
2016	1540	70	1078	1000	1078	539
2017	1540	70	1078	1000	1078	539
2018	1540	70	1078	1000	1078	539
2019	1540	70	1078	1000	1078	539
2020	1540	70	1078	1000	1078	539

2.5 QUALITY DEVELOPMENT

A comprehensive analysis of MSOFC NDE methods was undertaken by Dr. Ellingson of ANL. These results were compiled in a document, entitled "Nondestructive Characterization Methods For Monolithic Solid Oxide Fuel Cells," ASE Document 93-66149, published April 1, 1993. A summary of the major findings of the study is presented in Table 2-11.

TABLE 2-7

**ANNUAL U.S. BASELOAD GENERATION SOFC
MW GROWTH AND 1994 \$ VALUE**

Year	Base FC (Mw)	SOFC Penetration, percent	SOFC Penetration, Mw	Plant \$, kw Constant	Total \$, MM Installed	Stack \$, MM at \$/kw 350
2001	0					
2002	0					
2003	0					
2004	0					
2005	0					
2006	0					
2007	0					
2008	0					
2009	166	100%	166	1600	266	58
2010	332	100%	332	1600	532	116
2011	512	100%	512	1600	818	179
2012	1023	100%	1023	1600	1637	358
2013	1023	100%	1023	1600	1637	358
2014	1705	100%	1705	1600	2728	597
2015	2046	100%	2046	1600	3274	716
2016	2387	100%	2387	1600	3819	835
2017	2728	100%	2728	1600	4365	955
2018	2728	100%	2728	1600	4365	955
2019	2728	100%	2728	1600	4365	955
2020	2728	100%	2728	1600	4365	955

Numerous finite-element stress models of a single cell, single-cell stack (shown in Figure 2-16), and two-cell stacks have been developed. These models were generated parametrically so that they could be easily modified. Some of the parameters are:

- (a) Stack height
- (b) Number of bars, buttons, or corrugations

Figure 2-15. Process Flow Diagram for a High Efficiency SOFC Power Plant

Figure 2-16. Single-Cell Stack Model Using Bars

- (c) Number of stacks
- (d) Dimensions of the stack
- (e) Materials within the stack
- (f) Mesh density of the model

Stresses caused by thermal expansion differences between the components in the cool-down part of manufacturing were calculated. The stress results in combination with the Robust Design method provided guidance regarding the thicknesses of materials, geometrical configuration, and required range of material properties.

The cool-down model was used to evaluate every new design concept proposed for fabrication. A thin-film electrolyte approach was evaluated and compared (see Table 2-12) to the 2:1:1 and 1:5:1 A/E/C geometries. A/E/C anode and cathode stresses are greatly reduced in such an approach. The highest stresses are predicted in the corrugated cathode.

TABLE 2-8
OPTIMIZED SOFC POWER PLANT PERFORMANCE

Process Unit	Process Unit Name	Power, kw ^(a)
Air compressor	COMP-1	$W = -92$
Natural gas compressor	COMP-2	$W = -4$
Water pump	PUMP	$W = 0$
Hydrogen compressor	COMP-3	$W = -3$
Exhaust fuel turbine	TURB-1	$W = 35$
Exhaust air turbine	TURB-2	$W = 76$
Solid oxide fuel cell	SOFC	$W = 1767$
Reformer heat duty	REFORMER	$Q = 110$
Steam generator	HX8	$Q = -279^{(b)}$
Fuel exhaust stream	18 (FUEL-OUT)	$m = 1585 \text{ kg/hr, } T = 91^\circ\text{C}$
Air exhaust stream	27 (AIR-OUT)	$m = 5958 \text{ kg/hr, } T = 100^\circ\text{C}$
Electrical efficiency, ϵ_e		72.7 percent
Total efficiency, ϵ_T		71.6 percent
(a) Negative W corresponds to required input power; positive Q corresponds to heat input.		
(b) 30 percent of this heat goes to producing W_{steam} .		

TABLE 2-9

SUPPLIER ESTIMATED BULK PRICES

Material	Previous Cost Study Price per kg	Supplier	New Estimated Price per kg	Average Price per Kg
Zirconia	\$9.00	AlliedSignal	\$45.00	\$50
		Magnesium Elektron	\$80.00	
		Rhone-Poulenc	\$40.00 to \$50.00	
		TAM	\$41.00 to \$48.00	
		TOSOH	\$55.00 to \$60.00	
		Trans-Tech	\$20.00 to \$50.00	
		Z-Tech	\$55.00 to \$66.00	
Lanthanum chromite	\$80.00	AlliedSignal	\$100.00	\$100
		Cerac	\$400.00	
		HUA	\$50.00 to \$60.00	
		Molycorp	\$26.00 to \$33.00*	
		Rhone-Poulenc	\$100.00	
		SSC	\$100.00 to \$125.00	
		Trans-Tech	\$60.00 to \$5.00	
Lanthanum manganite	\$80.00	AlliedSignal	\$100.00	\$100
		Cerac	\$400.00	
		HUA	\$40.00 to \$50.00	
		Rhone-Poulenc	\$100.00	
		SSC	\$100.00 to \$125.00	
		Trans-Tech	\$50.00 to \$65.00	
Nickelous oxide	\$4.50	Aldrich	**	\$25
		Alfa	**	
		Cerac	\$21.00	
		J. T. Baker	\$26.00 to \$35.00	
Anode additive	\$1.50	Alcoa	\$2.00	\$10
		Meller Optics	\$2.00	
Binder	\$3.50	Union Carbide	\$8.00	\$8
Plasticizer	\$3.50	Monsanto	\$2.00	\$2
Pore former	\$3.50	E M Science	\$20.00	\$10
* Required calcining and milling				
** Research lots only				

TABLE 2-10
ANNUAL OPERATING COSTS (UPDATED)

	Southwest		Northeast	
	Coflow, \$M	Crossflow, \$M	Coflow, \$M	Crossflow, \$M
Labor	6.635	8.701	12.503	14.939
Equipment lease	0.050	0.050	0.050	0.050
Grounds upkeep	0.050	0.050	0.050	0.050
Maintenance	0.250	0.250	0.250	0.250
Raw materials	14.484	44.486	14.484	44.486
Utilities	5.000	5.000	7.000	7.000
Tax and insurance	1.000	1.000	2.000	2.000
Depreciation	1.701	2.096	1.802	2.228
Total	29.170	61.633	38.139	71.003

TABLE 2-11

SUMMARY OF POSSIBLE NDC METHODS

Process Step (for material)	Starting Materials (powders) - SrLaMnO ₃ LaCrO ₃	Blended Materials	Flat As-Cast Green Tapes		Corrugated Green Tapes (formed channels)	De- binding	Sintering	Non- manifolded Sintered Stack	Manifolded Sintered Stack
			Single Layer	Trilayer					
Defect Types; Material Character	Powder character- istics	Uniformity of blend, surface chemistry	Thickness density	Density, thickness, cracks	Residual stresses		Onset of cracking	Cracks in electrolyte or interconnect delamina- tions	Gas leakage
NDC Methods Suggested		¹ H NMR spectroscopy	•Acoustic microscopy (two-sided) •Low-kV through- transmission X-ray •Infrared imaging		FTIR, Raman Spectro- scopy		Acoustic emission	Acoustic resonance, optical Holography, optical borescopes	Gas pressure by H ₂ leak detection
Priority	High	Medium	Medium	Medium	Medium	High	Highest	Medium	Low

TABLE 2-12
STRESS ANALYSIS RESULTS

Factor	Thin Electrolytes*				2:1:1*	1:5:1*
Trapezoid side ratio	0.2	0.2	0.2	0.2	0.2	0.2
Anode thickness	0.005	0.005	0.007	0.007	0.005	0.0014
Electrolyte thickness	0.0005	0.0002	0.0005	0.0002	0.0025	0.0072
Cathode thickness	0.005	0.005	0.003	0.005	0.0025	0.0014
Corrugation thickness	0.010	0.010	0.010	0.010	0.010	0.010
Corrugation height	0.050	0.050	0.050	0.050	0.050	0.050
Flat anode thickness	0.010	0.010	0.010	0.010	0.010	0.010
Flat cathode thickness	0.010	0.010	0.010	0.010	0.010	0.010
Location	Maximum Stress**					
	Ksi	Ksi	Ksi	Ksi	Ksi	Ksi
Anode	15.6	15.3	12.9	12.8	18.1	24.8
Electrolyte	-25.1	-25.6	-29.9	-27.1	-25.0	-21.2
Cathode	9.2(-13.9)	9.1(-14.6)	7.5(-16.4)	8.0(-14.5)	13.3	12.5
Corrugated cathode	11.3	11.3	12.6	13.2	11.4	11.7
Corrugated anode	6.9(-12.2)	6.7(-11.7)	6.1(-10.5)	6.1(-12.4)	8.0(-14.5)	19.4(-20.7)

*Thickness and height in inches.

** Negative values indicate compressive stresses.

3. MATERIALS RESEARCH AND DEVELOPMENT

The manifolded MSOFC stack consists of multiple layers of materials which must simultaneously conform in their dynamic sintering characteristics and thermal expansion characteristics across a very broad temperature range. Failure to achieve a high degree of conformance can lead to deformation of the stack, cracking of the components, and delamination of the layers. In large stacks, loss of strength following "binder burnout" can cause serious deformation of the stack. Additionally, the various components must be compatible with the operational environment of the fuel cell. This includes compatibility with fuel and/or oxidant at the high operating temperature of the cell.

The central issue associated with a single thermal processing cycle for the set of MSOFC materials selected is the development of a lanthanum chromite interconnect material which sinters simultaneously with the electrode materials. The effort focused on this task is described in para. 3.2. Some success was achieved in this area via the use of "A" site and "B" site dopants in lanthanum chromite which produce a liquid phase, causing the lanthanum chromite to sinter at a lower temperature, compatible with the balance of the MSOFC materials. However, the doped lanthanum chromite did not fully densify when simultaneously fired in contact with both electrodes.

Additionally, it was found that this interconnect formulation, when separately fired and bonded in the stack, expanded and weakened in the presence of hydrogen, apparently leading to performance-compromising defects in the MSOFC stack.

On the positive side it has been found possible to design a manifolded MSOFC stack from separately fired and subsequently bonded components that has good thermal expansion matching of the components and can be repeatedly thermally cycled in air with no apparent adverse effects.

3.1 MATERIALS ASSESSMENT

The sintered properties of MSOFC components, the coefficients of thermal expansion of MSOFC components, the shrinkage characteristics of the anode in hydrogen and the expansion characteristic of the interconnect in hydrogen are reviewed below. Additionally, specific characteristics of the interconnect materials developed are reviewed separately in para. 3.2 and those of the electrolyte are reviewed in para. 3.5.

3.1.1 Sintered Characteristics of MSOFC Components

The final measurements made of the average sintered properties of baseline anode and cathode batches are compiled in Table 3-1.

TABLE 3-1				
AVERAGE SINTERED PROPERTIES OF MSOFC BATCHES				
Baseline Batch	Diametral Shrinkage, Percent	Weight Loss, percent	Density, g/cc	Theoretical Density, percent
A11191-1	17.7 $\pm$ 0.9	23.1 $\pm$ 0.1	4.38 $\pm$ 0.18	71.5 $\pm$ 3.0
A11201-1	17.6 $\pm$ 1.0	22.9 $\pm$ 0.1	4.48 $\pm$ 0.09	73.1 $\pm$ 1.5
A11201-2	19.6 $\pm$ 0.5	22.6 $\pm$ 0.2	4.33 $\pm$ 0.13	70.7 $\pm$ 1.9
A11211-1	19.3 $\pm$ 1.3	22.9 $\pm$ 0.2	4.43 $\pm$ 0.11	72.2 $\pm$ 1.8
CE03122-1	21.2 $\pm$ 0.5	23.7 $\pm$ 0.2	5.00 $\pm$ 0.10	79.7 $\pm$ 1.6
CE03132-1	22.0 $\pm$ 0.3	24.0 $\pm$ 0.2	4.88 $\pm$ 0.15	77.7 $\pm$ 2.4
CE03132-2	21.2 $\pm$ 0.6	23.5 $\pm$ 0.1	4.86 $\pm$ 0.17	77.4 $\pm$ 2.7

Figure 3-1 shows the properties of baseline anode batches measured during the course of the program. Figure 3-2 shows the properties of baseline cathode batches measured during the course of the program. Both show relatively small variances in the properties measured.

Two high solids loading anode batches were prepared. High solids loading anodes were used to fabricate flat anode plates in certain cell constructions. A small anode batch (A01072-1) of high solids loading was first prepared using the torque rheometer. Based on the favorable results of the torque rheometer batch, a larger batch (A01172-1) was then prepared using the Banbury mixer. The average sintered properties of these anode batches are given in Table 3-2.

Figure 3-3 compares the properties of these batches with a previously prepared high solids loading batch (A07030-1) and other baseline batches.

Other batches were made in an effort to improve the structural performance of the baseline batches. The primary objective was to decrease the magnitude and frequency of defects in modules and stacks. The approach was to toughen the baseline materials. Toughening was accomplished by replacing portions of the zirconia components with alumina in each of the anode, electrolyte, and cathode formulations. The addition of alumina has been shown to increase the strength and toughness of stabilized zirconia in previous work. Modified anode (A10241-1), electrolyte (E1024-1), and cathode (CE11071-1 and CE 11071-2) batches were prepared based on this toughening approach. An anode batch (A01282-1) was prepared with the addition of alumina and with no pore former for the interconnect work in an effort to control the pore volume and firing shrinkage of the anode and wicking in the interconnect. In addition, a Banbury batch of alumina-modified cathode (CE01212-1) was made. The properties of these batches are shown in Table 3-3.

Figure 3-1. Properties of Baseline Anode Batches

Figure 3-2. Sintered Properties of Baseline Cathode Batches

TABLE 3-2				
AVERAGE PROPERTIES OF HIGH SOLIDS LOADING ANODE BATCHES				
Batch	Diametral Shrinkage, %	Weight Loss, %	Density, g/cc	Theoretical Density, %
A01072-1	17.2±0.4	21.8±0.0	4.64±0.08	75.6±1.3
A01172-1	16.9±0.4	21.6±0.1	4.48±0.13	73.1±2.1

Figure 3-3. Sintered Properties of High Solids Loading Anodes (50 vol % Solids) vs Baseline Anodes (47 vol % Solids)

Using X-ray diffraction, the phase compositions of the modified materials were evaluated and compared to the baseline materials. Table 3-4 shows the phase compositions of the baseline and modified batches. In the anode layer, all of the alumina (in both the baseline and the modified material) reacts with nickelous oxide to form a nickel aluminate phase; the zirconia remains as a separate phase in the anode. In the electrolyte layer, the zirconia and alumina remain as separate phases. In the cathode layer the lanthanum zirconate phase, which is seen in the baseline, is suppressed by the formation of a manganese aluminate phase in the modified material.

TABLE 3-3				
AVERAGE PROPERTIES OF MODIFIED BATCHES				
Modified MSOFC Batch	Diametral Shrinkage, Percent	Weight Loss, percent	Density, g/cc	Theoretical Density, percent
A10241-1	16.5 ± 0.5	23.5 ± 0.1	4.15 ± 0.06	69.9 ± 1.1
E10241-1	13.2 ± 0.1	17.8 ± 0.1	5.43 ± 0.05	99.9 ± 0.9
CE11071-1	22.4 ± 0.8	24.6 ± 0.1	5.14 ± 0.18	85.5 ± 3.0
CE11071-2	22.2 ± 0.4	24.8 ± 0.1	5.05 ± 0.17	83.9 ± 2.8
A01282-1	15.6 ± 0.4	18.7 ± 0.0	4.69 ± 0.11	79.4 ± 1.8
CE01212-1	21.7 ± 0.3	24.4 ± 2.8	5.21 ± 0.07	8.6 ± 1.2

TABLE 3-4		
PHASES PRESENT IN BASELINE AND MODIFIED MSOFC BATCHES		
	Baseline	Modified
Anode (A)	NiO ZrO ₂ NiAl ₂ O ₄	NiO ZrO ₂ NiAl ₂ O ₄
Electrolyte (E)	ZrO ₂	ZrO ₂
Cathode/electrolyte (CE)	ZrO ₂ LaMnO ₃ La ₂ Zr ₂ O ₇	ZrO ₂ LaMnO ₃ Mn ₂ AlO ₄

3.1.2 MSOFC Component Thermal Expansion Data

Coefficients of thermal expansion (CTE) data were generated for anode, cathode, interconnect, and electrolyte tapes. A Linseis differential dilatometer was used in determining the respective coefficients. Sample preparation entailed cutting out 8.8 mm x 25.4 mm pieces of green tape. The sample was then wound around a 3.3-mm alumina rod and simply slipped off, forming a hollow cylindrical geometry. The tape is kept from unwinding using scotch tape. Green samples are then placed in the furnace and de-bindered over a two-day firing cycle. Samples reach a maximum temperature of 1350°C and are held at this temperature for 30 min. Generally, five samples are made per composition, and three are run. The firing rate used in determining expansion coefficients is 3°C per minute to 1000°C. After the samples are run, an average value is determined along with standard deviation.

In the final selected stack configuration the key components are the anode and interconnect. The stack consists of anode, electrolyte, cathode, and interconnect materials. However, with the thin-electrolyte cell construction and the utilization of interconnect bars instead of cathode bars to conduct current through the air channels, the electrolyte and cathode do not play a major role in the thermomechanical structural effects. Consequently, thermal expansion matching of the interconnect and the anode are key to successful thermal cycling of the stack in air.

The close thermal expansion match between two of the anode formulations and the baseline calcium-, cobalt-doped lanthanum chromite interconnect is shown in Figures 3-4 and 3-5. Although there is some divergence at lower temperatures, the expansions of the anodes and interconnects are matched at 1000°C to 0.02 percent or less. Stacks fabricated with these materials showed remarkable resistance to stress-induced defects through numerous thermal cycles.

Because the baseline interconnect expands in hydrogen, several other interconnect formulations were examined for the effects of hydrogen on the expansion of the material. The CTE's for these materials are shown in Table 3-5.

The average CTE of the baseline electrolyte over the range of 20° to 1000°C was measured to be 10.17×10^{-6} per 1°C. The average CTE of the baseline cathode over the range of 20° to 1000°C was measured to be 10.50×10^{-6} per 1°C.

3.1.3 Expansion of the Interconnect in Hydrogen

During the latter stages of the project it was found that exposure of the baseline interconnect to hydrogen caused expansion and weakening of the material. The expansion of the baseline interconnect and the experimental method are shown in the data presented in Figure 3-6. The interconnect was heated in a nitrogen atmosphere to 1000°C where it was allowed to soak for approximately 15 min to permit temperature stabilization. Subsequently, hydrogen was introduced to the atmosphere at 10 percent and the sample was allowed to soak at 1000°C for approximately 60 min. Following the soak, the hydrogen flow was terminated and the sample exposed to air at 1000°C.

As shown in Figure 3-6, there is a 0.159-percent expansion following exposure of the sample to hydrogen. With exposure to high-temperature air the sample returns to nearly its original length. Similar effects have been observed with a number of candidate interconnect materials. A compilation of the measured expansion of a number of interconnect materials is presented in Table 3-6. Most of these materials show unacceptably high expansion and/or CTE values too low to match the anode materials. Further development effort in this area is clearly required.

Based on XRD analysis, lattice parameter measurements were made for powder samples of undoped, calcium-, cobalt-doped and strontium-doped lanthanum chromite. Table 3-7 shows that the lattice constant changes upon exposure to hydrogen. As shown by the data, the lattice parameters of the undoped lanthanum chromite remain relatively unchanged while those of the doped lanthanum chromite materials show a significant expansion. Table 3-8 presents strain calculations based on the lattice

Figure 3-4. CTE/CTC of Anode No. 1 and Interconnect

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Figure 3-5. CTE/CTC of Anode No. 2 and Interconnect

B-28964

TABLE 3-5	
CTE DATA FOR LANTHANUM CHROMITE COMPOSITIONS	
Composition	CTE ($10^{-6}/^{\circ}\text{C}$)
LaCrO_3	9.21
$\text{La}_{0.82}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (baseline)	11.4
$\text{La}_{0.8}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{Co}_{0.05}\text{O}_3$	11.47
$\text{La}_{0.85}\text{Ca}_{0.15}\text{Cr}_{0.95}\text{Co}_{0.05}\text{O}_3$	10.96
$\text{La}_{0.85}\text{Ca}_{0.15}\text{Cr}_{0.93}\text{Co}_{0.07}\text{O}_3$	11.13
$\text{LaCr}_{0.7}\text{Mg}_{0.3}\text{O}_3$	10.47
$\text{LaCr}_{0.97}\text{Co}_{0.03}\text{O}_3$	10.20
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.85}\text{Zn}_{0.15}\text{O}_3$	10.72

constant changes. Table 3-9 shows possible stresses created by the material expansion. Clearly, the observed weakening of the doped lanthanum structure is to be expected.

3.1.4 Contraction of the Anode Upon Exposure to Hydrogen

Also during the latter stages of the project it was found that there was a significant contraction of the anode material upon exposure to hydrogen due to the reduction process. This is shown in Figure 3-7 where a contraction of 0.34 percent in the baseline anode material was observed. This problem has been largely solved by changing the additives to the anode. The contraction exhibited by the anode formulation used for electrode bars in the last few stacks fabricated is shown in Figure 3-8. A contraction of less than 0.04 percent was observed – satisfactory for operation of the stack.

3.2 STUDY OF INTERCONNECT/CATHODE INTERACTION

The ultimate goal of MSOFC technology is to develop a process for fabricating manifolded MSOFC stacks which requires only one thermal processing cycle. A key issue in the development of a manifolded MSOFC stack, which is fired in a single thermal processing cycle, is the development of a suitable ceramic interconnect. The interconnect material chosen for this program was lanthanum chromite.

Experience in previous projects had shown that lanthanum chromite failed to densify in air at temperatures low enough to be compatible with the thermal processing of the other MSOFC components. Liquid phase sintering aids used in previous projects tended to migrate to other parts of the fuel cell structure and react with other components, causing elemental migration and morphological changes. In this project several approaches were taken to resolve the interconnect issue. Several lanthanum chromite

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Figure 3-6. Effect of H₂ Reduction on Baseline Interconnect

TABLE 3-6	
EXPANSION OF INTERCONNECT MATERIALS IN HYDROGEN	
Composition	Expansion in 10% H ₂ (%)
LaCrO ₃	0.016
La _{0.82} Ca _{0.2} Cr _{0.9} Co _{0.1} O ₃	0.159
La _{0.8} Sr _{0.1} Cr _{0.95} Co _{0.05} O ₃	0.105
La _{0.85} Ca _{0.15} Cr _{0.95} Co _{0.05} O ₃	0.114
La _{0.85} Ca _{0.15} Cr _{0.93} Co _{0.07} O ₃	0.123
La _{0.8} Sr _{0.1} CrO ₃	1.030*
LaCr _{0.7} Mg _{0.3} O ₃	0.147
LaCr _{0.97} Co _{0.03} O ₃ (2/4&5/)	0.017
La _{0.85} Sr _{0.15} Cr _{0.85} Zn _{0.15} O ₃	0.067
*This expansion is unusually high; duplicate runs have not been made.	

TABLE 3-7			
LATTICE CONSTANT CHANGES OF LANTHANUM CHROMITES UPON EXPOSURE TO HYDROGEN AT 1000°C (BEFORE/AFTER)			
Material	A Axis (Å)	B Axis (Å)	C Axis (Å)
LaCrO ₃	5.4982/5.4987	5.5157/5.5153	7.7781/7.7784
(La,Ca)(Cr,Co)O ₃	5.4601/5.4663	5.4750/5.4869	7.7255/7.7413
(La,Sr)CrO ₃	5.4811/5.4812	5.5066/5.5098	7.7501/7.7656

TABLE 3-8			
STRAIN CALCULATION FOR LANTHANUM CHROMITE MATERIALS EXPOSED TO HYDROGEN (DATA TAKEN FROM PEAK AROUND 78°2θ)			
Material	d ₀ (Å)	d _H (Å)	Strain
LaCrO ₃	1.2277	1.2269	-0.000650
(La,Ca)(Cr,Co)O ₃	1.2193	1.2214	0.001722
(La,Sr)CrO ₃	1.2257	1.2261	0.000326

TABLE 3-9		
CALCULATION OF POSSIBLE STRESSES CREATED BY MATERIAL EXPANSION UPON EXPOSURE TO HYDROGEN AT 1000°C (STRAIN DATA FROM TABLE 3-8)		
Material	Strain (Exp)	Stress (Exp)
(La,Ca)(Cr,Co)O ₃	0.001722	-950 MPa
(La,Sr)CrO ₃	0.000326	-180 MPa

compositions densified when fired alone in air and some densified when fired with anode material. However, none showed completely satisfactory results when fired in the anode/interconnect/cathode trilayers necessary for successful stack fabrication. Although none of the approaches was completely successful, considerable progress was made and a much deeper understanding of the processing of the interconnect in the fuel cell stacks was achieved.

Although this task effort was centered at Argonne National Labs, a small parallel effort was performed at ASE. Basically, three different approaches were taken as follows:

- (g) ANL explored an approach involving a two-material cell, consisting of interconnect and electrolyte materials only. Because such a cell contains no lanthanum manganite, more severe conditions (higher sintering temperature or more reducing gas atmosphere) can be used to densify the interconnect.
- (h) ANL pursued an approach to manage the interaction between the interconnect liquid phase and electrodes to obtain high density in the conventional four-material cell.
- (i) ASE developed techniques for managing the effects of liquid phase formation via various arrangements of the fuel cell component layers.

The results of these approaches are reviewed next.

3.2.1 Two-Material Effort at ANL

In the two-material MSOFC, the cathode and anode of cathode-electrolyte-anode composites are made from interconnect material; these layers must remain porous during firing. At the same time, the interconnect and electrolyte layers must densify nearly completely. In addition, strong bonds must be formed between the electrolyte and electrodes and between the interconnect and electrodes. The electrolyte composites made using interconnect material (La_{0.8}Ca_{0.22}Cr_{0.9}Co_{0.1}O₃) as the electrodes had both dense electrolyte and porous electrodes. However, the bonding

Figure 3-7. Contraction of Baseline Anode Upon Reduction in H₂

Figure 3-8. Contraction of Modified Anode Upon Reduction in H_2

between the electrolyte and electrodes was very weak, as seen by the fact that the electrodes detached from the electrolyte in several cases.

To improve bonding between the electrodes and electrolyte, electrolyte composites were tape cast with electrodes that consisted of 10-, 20-, or 30-wt% partially stabilized zirconia (6 mol% Y_2O_3) mixed with the interconnect material. All composites were fired for 1/2 hr at 1400°C in air. Bonding in the 10- and 20-percent composites was weak, and the electrodes detached from the electrolyte when samples were broken for microscopic examination. Bonding was stronger in the 30-percent composite, and the electrodes did not detach. Figure 3-9 focuses on one of the electrolyte/electrode boundaries in the 30-percent composite, and shows that the electrolyte is dense while the electrode is porous, as desired. However, the boundary between electrolyte and electrode is sharp, suggesting that the bonding might be weak and that it could be improved further. To improve bonding, more zirconia was added to the electrodes, in the amount of 35- and 40-wt% partially stabilized zirconia. Figure 3-10 shows that distinct boundaries still exist between the electrolyte and electrodes of the 40-percent composite, suggesting that more zirconia might be necessary. However, addition of too much zirconia might degrade the electrochemical performance of the composites.

Figure 3-9. Interface of the 30-Percent Composite Showing Dense Electrolyte and Porous Electrode

There must also be a strong bond between the electrodes and the interconnect. To test the bonding between interconnect and electrodes, five-layer composites (LC/EI/Zy/EI/LC) were tape cast, where LC is 100 percent $La_{0.8}Ca_{0.22}Cr_{0.9}Co_{0.1}O_3$, E is 65-wt% $La_{0.8}Ca_{0.22}Cr_{0.9}Co_{0.1}O_3$ /35-wt% TZ-3Y, and Zy is 70-wt% TZ-8Y/30-wt% TZ-3Y. These

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Figure 3-10. 40-Percent Composite with Dense Electrolyte and Porous Electrode

composites were fired at 1400°C in air for 1/2 hr. All composites were intact after firing, suggesting that bonding is sufficiently strong for fabrication of a two-cell stack.

Bonding in electrolyte composites was improved by using a five-layer graded structure, rather than the three-layer structure. Two different five-layer composites were made by co-casting, with the only difference being in the inner bond layers; the other layers were the same. In composite 1, the bond layers contain 80% ZrO_2 /20%LC whereas the bond layers of composite 2 contain 65% ZrO_2 /35%LC. The makeups of these composites are given below:

Composite 1	Composite 2
35% ZrO_2 /65%LC	35% ZrO_2 /65%LC
80% ZrO_2 /20%LC	65% ZrO_2 /35%LC
100% ZrO_2	100% ZrO_2
80% ZrO_2 /20%LC	65% ZrO_2 /35%LC
35% ZrO_2 /65%LC	35% ZrO_2 /65%LC

Composites 1 and 2 were fired at temperatures of 1400°, 1500°, and 1600°C for 1/2 hr in air; then the bonding was evaluated by scanning electron microscopy on polished cross-sections. For comparison, the following three-layer composites were fired at the same temperatures:

<u>Composite 3</u>	<u>Composite 4</u>
30%ZrO ₂ /70%LC	40%ZrO ₂ /60%LC
100%ZrO ₂	100%ZrO ₂
30%ZrO ₂ /70%LC	40%ZrO ₂ /60%LC

Figure 3-11 shows micrographs of composite 1 fired at 1400°C. Figure 3-11a shows the overall view of the composite, and Figures 3-11b and 3-11c show magnified views of the interfaces between the various layers. The large cracks seen in Figure 3-11a are results of the specimen mounting procedure. Such cracks disappeared when the mounting procedure was changed. The large vertical crack on the left side of the composite suggests that the bonding between layers is good, because the crack runs through the outer layer rather than along the interface. This indicates that the bond is stronger than the material of the outer layer. Figure 3-12 shows similar views of composite 1 fired at 1500°C. Bonding appears to be good, and, because the polishing procedure was changed, no cracks are evident.

Figure 3-13 shows composite fired at 1400°, 1500°, and 1600°C. Composite 4 is expected to have the best bonding of the three-layer composites, because it contains the most ZrO₂ in the electrode layer, but a sharp boundary is evident between the electrode and electrolyte layers, even when the composite is fired at 1600°C. This suggests that the bonding remains weak in three-layer composites even when they are fired at high temperature.

Ac impedance was used to test the electrochemical performance of the LC electrode/YSZ/LC electrode (IEI) composites in reducing (H₂/H₂O) and oxidizing (air) atmospheres. The results are summarized in Table 3-10. Past results from tests performed on IEI cells without the intermediate doped LaCrO₃/YSZ layer and without YSZ in the electrode are shown for comparison. (NO TAG)

Microscopic examination of the interfacial regions in the composites indicates that the addition of YSZ to the electrode improves the electrode/electrolyte bonding. This improved bonding is reflected in the drop in interfacial impedance between IEI and IEI-8. However, this decrease in interfacial impedance is partially offset by an increase in bulk impedance resulting from the relatively poor conductivity of the doped LaCrO₃/YSZ mixture compared to pure doped LaCrO₃ (0.89 ohm⁻¹cm⁻¹ vs 31.1 ohm⁻¹cm⁻¹). (NO TAG)

The addition of an intermediate 80-wt% (IEI-15) or 65-wt% (IEI-16) YSZ layer decreases the total cell resistance by 49 and 33 percent, respectively. As shown in Table 3-10, the drop in total cell impedance can be attributed mainly to a decrease in the bulk impedance rather than in the interfacial component. A significant difference between IEI-15 and IEI-8 lies in the thickness of the YSZ electrolyte layer. The electrolyte layer thickness in IEI-15 is 74 μm vs 103 μm for IEI-8. However, the addition of the 80-wt% YSZ intermediate layers to IEI-15 increases the total thickness of layers between the electrodes (162 μm) to more that of IEI-8. Since the electrode thicknesses are identical in the two cells, the lower bulk impedance of IEI-15 indicates that 80-wt%

A. Overall Composite

B. Interface Between Electrolyte (left) and Bond Layer Containing 80% ZrO_2 (right)

C. Interface Between Layer Containing 80% ZrO_2 (left) and Electrode with 35% ZrO_2 (right).

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Figure 3-11. Micrographs of Composite 1 Fired at 1400°C Showing Improved Bonding Between Electrolyte and Electrodes

A. Overall Composite

B. Interfaces Between Electrolyte (left layer), Bond Layer with 80% ZrO_2 (middle layer), and Electrode with 35% ZrO_2 (right layer).

Figure 3-12. Micrographs of Composite 1 fired at 1500°C

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A. Fired at 1400°C

B. Fired at 1500°C

C. Fired at 1600°C, Showing a Sharp Boundary Between Electrolyte and Electrodes

F-66171

Figure 3-13. Micrographs of Composite 4 (40% ZrO_2 in Electrodes)

TABLE 3-10

AREA-SPECIFIC RESISTANCE (OHM-CM²) OF IEI COMPOSITES AT 1000°C

Sample	Air Atmosphere		H ₂ /H ₂ O Atmosphere		Air and H ₂ /H ₂ O		Total
	Interfacial	Bulk	Interfacial	Bulk	Interfacial	Bulk	
IEI	0.184	0.484	2.91	1.10	3.58	0.801	4.38
IEI-8	0.109	1.17	1.40	2.79	1.63	2.11	3.74
IEI-15	0.124	0.475	0.790	1.16	1.01	0.905	1.91
IEI-16	0.148	0.356	1.48	1.58	1.62	1.17	2.51
IEI-18	0.149	0.415	1.04	1.32	1.35	0.940	2.29
IEI-19	0.100	0.915	0.678	1.18	(0.780)	(1.05)	(1.83)

() = Calculated from single atmosphere results.

Compositions:

IEI: doped LaCrO₃, YSZ, doped LaCrO₃.

IEI-8: 35 wt% YSZ/65 wt% doped LaCrO₃, YSZ, 35 wt% YSZ/65 wt% doped LaCrO₃.

IEI-15,18,19: 35 wt% YSZ/65 wt% doped LaCrO₃, 80 wt% YSZ/20 wt% doped LaCrO₃, YSZ, 80 wt% YSZ/20 wt% doped LaCrO₃, 35 wt% YSZ/65 wt% doped LaCrO₃.

IEI-16: 35 wt% YSZ/65 wt% doped LaCrO₃, 65 wt% YSZ/35 wt% LaCrO₃, YSZ, 65 wt% YSZ/35 wt% LaCrO₃, 35 wt% YSZ/65 wt% doped LaCrO₃.

YSZ/20-wt% doped LaCrO₃ is more conductive than pure YSZ. The same conclusion can be reached about the conductivity of 65-wt% YSZ/35-wt% doped LaCrO₃ by comparing IEI-16 and IEI-8.

By comparing the data presented for IEI-15, 16, and 18 to the data for IEI-8, it is evident that the benefit of the intermediate bonding layers in reducing the interfacial impedance is marginal compared to their contribution to the bulk impedance. In terms of a two-material fuel cell, the best compromise between decreasing the interfacial impedance and minimizing an addition to the bulk impedance is a three-layer cell with YSZ/doped LaCrO₃ electrodes and as thin an electrolyte layer as possible.

The total cell impedance has been further reduced by decreasing the thicknesses of all five layers. The thicknesses of the YSZ, 80-wt% YSZ, and 35-wt% YSZ layers have been reduced by 34, 37, and 43 percent, respectively, in IEI-18 and IEI-19, as compared to IEI-15. The best total cell impedance obtained to date is 1.83 ohm-cm².

The single atmosphere results presented in Table 3-10 consistently show the impedances in reducing atmospheres to be higher than those in oxidizing atmospheres. This supports the conclusion that the doped LaCrO₃/YSZ mixture is a satisfactory cathode material but an unsatisfactory anode material.

3.2.2 Four-Material Effort at ANL

The LaCrO_3 interconnect does not completely densify in the usual four-material MSOFC because the liquid that aids sintering migrates into the electrodes before densification is complete. To improve densification, an attempt is being made to increase the amount of liquid phase present during sintering, so that migration of some liquid does not significantly affect densification. In the past, attempts to increase the amount of liquid phase included the addition of CaCrO_4 , which melts at $\sim 1200^\circ\text{C}$ according to the phase diagram. It has been reported that CaCrO_4 is not useful for this purpose, however, because it forms Cr_2O_3 , which coats the grain boundaries and inhibits densification. It has also been reported that compositions closer to the 1022°C eutectic would be more useful for this purpose. To prevent migration of the liquid phase before sintering can proceed, the liquid phase should not form until the sintering temperature has been reached ($\sim 1200^\circ\text{C}$). According to the phase diagram, the "941" composition exhibits a local maximum in melting point (1288°C in oxygen), and may be ideal. For this reason, the "941" composition was prepared for use as a sintering aid.

"941" was tested as a sintering aid for Ca/Co-doped LaCrO_3 . In this work, "941" was added to Ca/Co-doped LaCrO_3 deficient in calcium, so that a final composition of $\text{La}_{0.70}\text{Ca}_{0.30}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$ was obtained after sintering/reaction. Formation of LaCrO_3 containing excess calcium or lanthanum was intentionally avoided, because such material is expected to be unstable and susceptible to hydrolysis reactions. The amounts of "941" added and the initial Ca/Co-doped LaCrO_3 compositions are given below:

x	y	a	b	c
0.94	0.025	0.74	0.24	0.11
0.89	0.050	0.79	0.17	0.11
0.83	0.075	0.84	0.09	0.12
0.78	0.100	0.90	0.00	0.13

Precursors of the various LaCrO_3 compositions and "941" were made by the liquid-mix method. The "941" precursor was calcined for 24 hr at 975°C in air, whereas the LaCrO_3 precursors were calcined for 24 hr at 750°C in air. The appropriate amounts of $\text{LaCrO}_3(\text{X})$ and "941"(Y) were mixed with mortar and pestle. Then pellets were pressed and fired according to the schedules given below. To determine the effectiveness of "941" as a sintering aid, each LaCrO_3 composition was also fired without any "941" added. To this point, "941" has been tested with two Ca-deficient compositions: $\text{La}_{0.79}\text{Ca}_{0.17}\text{Cr}_{0.90}\text{Co}_{0.11}\text{O}_3$ and $\text{La}_{0.90}\text{Ca}_{0.00}\text{Cr}_{0.90}\text{Co}_{0.13}\text{O}_3$. It has also been tested with $\text{La}_{0.80}\text{Ca}_{0.22}\text{Cr}_{0.90}\text{Co}_{0.10}\text{O}_3$, the composition with a slight Ca excess that has been shown to densify alone but not in composite tapes. The results of this study are given in Table 3-11.

TABLE 3-11				
RESULTS OF STUDY EXPLORING THE POSSIBLE USE OF "941" AS SINTERING AID FOR Ca/Co-DOPED LaCrO ₃				
LaCrO ₃ Composition	Heat Treatment	Moles LaCrO ₃	Moles "941"	Density, g/cm ³
La _{0.79} Ca _{0.17} Cr _{0.90} Co _{0.11} O ₃	1400°C/1 hr	0.89	0.00	2.65
"	"	0.89	0.05	3.97
"	1020°C/2 hr 1400°C/1 hr	0.89	0.00	2.69
"	"	0.89	0.05	3.88
"	1500°C/1 hr	0.89	0.00	2.85
"	"	0.89	0.05	4.11
"				
La _{0.90} Ca _{0.00} Cr _{0.90} Co _{0.13} O ₃	1400°C/1 hr	0.78	0.00	3.21
"	"	0.78	0.10	3.98
"	1500°C/1 hr	0.78	0.00	3.24
"	"	0.78	0.10	4.25
"				
La _{0.80} Ca _{0.22} Cr _{0.90} Co _{0.10} O ₃	1400°C/1 hr	1.00	0.00	6.1-6.2
"	"	0.95	0.05	5.21
"	"	0.90	0.10	4.57

Comparing the densities of Ca-deficient compositions with no "941" added, to the same compositions with "941" added shows that "941" aids densification to a certain degree, but the final densities are still too low for the MSOFC. For example, the density of La_{0.79}Ca_{0.17}Cr_{0.90}Co_{0.11}O₃ increases substantially from 2.65 to 3.97 g/cm³, but this density is still very low for the interconnect. Comparing the density of La_{0.79}Ca_{0.17}Cr_{0.90}Co_{0.11}O₃ to that of La_{0.80}Ca_{0.22}Cr_{0.90}Co_{0.10}O₃ shows that a very slight decrease in the Ca content causes a drastic decrease in density from ≈6.1 to 2.65 g/cm³. This is consistent with the idea that it is a Ca-rich liquid which aids densification in La_{0.80}Ca_{0.22}Cr_{0.90}Co_{0.10}O₃. When La_{0.80}Ca_{0.22}Cr_{0.90}Co_{0.10}O₃ is fired in composite tapes, migration of the Ca-rich liquid leaves a Ca-deficient material that densifies poorly. On the other hand, addition of "941" to La_{0.80}Ca_{0.22}Cr_{0.90}Co_{0.10}O₃ causes a decrease in its density, suggesting that the stoichiometry must be tightly controlled to obtain highly dense material. If the density is in fact strongly dependent on the Ca content, then addition of "941" to La_{0.80}Ca_{0.22}Cr_{0.90}Co_{0.10}O₃ in composite tapes might be a method for replacing calcium that is lost by migration of the liquid phase.

Another approach was attempted in order to limit migration of the transient liquid phase from the interconnect in the standard four-material cell. The method for limiting migration is to delay liquid formation until after the onset of densification for the electrodes ($\approx 1050^\circ\text{C}$), because the migration paths are reduced when these layers are relatively dense. By replacing calcium with strontium to give an interconnect composition of $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$, the liquid formation temperature is expected to increase from $\approx 1020^\circ\text{C}$ to $\approx 1250^\circ\text{C}$.

Two trilayer tapes (AIA and CIC) were made to test the densification of $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ in composite tapes. In these and all subsequent representations of composite tapes, A represents the anode, I the interconnect, and C the cathode. Symmetric trilayers were made, rather than an AIC, to avoid problems with a shrinkage mismatch. The trilayers were fired in air at 1500°C for 1 hr. After firing, fracture surfaces of the trilayers were examined by SEM. Figures 3-14a and 3-14b show that the interconnect densified well in the AIA. Figure 3-15a shows that a dense layer also formed in the CIC, but the dense layer was thin, and interaction between the interconnect and cathode was still evident. Figure 3-15b shows a second CIC in which the interconnect was not completely dense, but its density was higher than in the trilayers made with $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$. These figures show that $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ shows promise as an interconnect material, but interactions, primarily with the cathode, still hinder its complete densification in trilayers.

To test new cell assemblies in which cathode/interconnect interactions might be reduced, Al's were fired with the interconnect layer contacting a corrugation made from either $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ or $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$. A cathode flat layer was laid on the other side of the corrugation in both cases to simulate the arrangement in an actual cell. Al's were also fired by themselves as a comparison. In all cases, the interconnect layer was $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$, and the assemblies were fired in air for 1 hr at 1500°C .

Figures 3-16a and 3-16b show the interconnect layer of an Al fired by itself. Although densification was not complete, the density was high, and testing showed the composite to be impervious to water, an indication that the porosity was not connected. Of the Al's fired in contact with corrugations, the interconnect densified best when in contact with the $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ corrugation. This might be expected, because the interconnect composite did not contact the cathode at all in this arrangement. Figure 3-17 shows the interconnect layer of an Al fired in contact with a $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ corrugation. The density of the interconnect in Figure 3-17 appears comparable to that in Figure 3-16, suggesting that densification of the interconnect is not significantly hindered in such a cell assembly. It further suggests that only slightly improved densification of the interconnect is necessary in such a cell assembly.

3.2.3 Study of $(\text{La,Ca})\text{CrO}_3$

The densification of perovskite lanthanum chromites has been extensively studied. Recently, Mori^(NO TAG) and others have fully densified calcium-doped lanthanum chromites at relatively low temperatures (1200° to 1400°C) by adding excess calcium. Their powder processing involved calcining above 1000°C , followed by grinding and reheating to obtain a single-phase solid solution of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ with $0.2 \leq x \leq 0.4$.

(a)

(b)

Figure 3-14. SEM Micrographs of AIA Fired at 1500°C in Air for 1 hr at Magnifications of (3-14a) ≈ 350 X and (3-14b) ≈ 2000 X

F-66172

(a)

(b)

Figure 3-15. SEM Micrographs of Two CIC's Fired at 1500°C in Air for 1 hr

F-66173

(a)

(b)

Figure 3-16. SEM Micrographs of Al Fired by Itself at 1500°C for 1 Hr in Air at Magnifications of (3-16a) ≈ 350 X and (3-16b) ≈ 1500 X

F-66174

F-66175

Figure 3-17. SEM Micrograph of Al Fired in Contact With $\text{La}_{0.8}\text{Sr}_{0.22}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Corrugation

This study was focused on lower-temperature powder preparation (800°C) and sintering (1050° to 1300°C) of $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$. (The powders intentionally were slightly chromium-rich to avoid the possible appearance of excess lanthanum compounds which would cause the mechanical integrity of the sintered component to degrade; this was also found to affect sinterability.) At calcining temperatures of 800°C or less, CaCrO_4 was found to coexist with $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$ for $x \geq 0.2$. However, CaCrO_4 is soluble at higher temperatures and dissolves into the matrix when sintered above its solubility limit. Since CaCrO_4 melts incongruently, its use as a liquid-phase sintering aid is restricted. However, the Ca-Cr-O system includes other compositions that may react and melt with the CaCrO_4 . In particular, the eutectic composition, $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and a calcium-rich ternary compound, $\text{Ca}_3(\text{CrO}_4)_2$ were investigated. Attempts were made to use these compositions to densify calcium-doped lanthanum chromites.

3.2.3.1 Experimental Procedures

3.2.3.1.1 Powder Processing

All powders were prepared using a modified Pechini method. Metal nitrates or carbonates were dissolved into water and nitric acid and then mixed with an ethylene

glycol/citric acid mixture having a mole ratio of 1:1:1. The solution was boiled to drive off water and nitrates and allowed to gel. The gel was then put in a drying oven at $\sim 120^{\circ}\text{C}$. As the gel dried, it foamed and charred. The char was milled and reheated to about 400°C to remove residual carbon. The resulting powders were then milled and calcined to various temperatures as needed.

3.2.3.2 Quench Study

$\text{La}_{0.99}\text{Ca}_{0.01}\text{CrO}_4$ powder prepared at 400°C and containing CaCrO_4 was isostatically pressed into 1.2-cm pellets at 210 MPa. Green densities approached 50 percent of the calculated theoretical density. The pellets were heated at a rate of $8^{\circ}\text{C}/\text{min}$ and quenched in water from the temperatures: 490° , 1075° , 1175° , 1230° , 1275° , 1350° , and 1400°C . One pellet was held at 1400°C for 2 hr and then furnace-cooled, and another was held at 1400°C for 3 min and then air-quenched.

Microanalysis and energy dispersive analysis were performed on fractured surfaces using a JEOL scanning electron microscope (SEM).

3.2.3.3 Thermal Analysis

Thermogravimetric and differential thermal analyses (TG/DTA) were performed on $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_4$ $0.1 \leq x \leq 0.4$, CaCrO_4 and $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ powders using a Netzsch TGA/DTA system. The furnace heating rate for each run was $10^{\circ}\text{C}/\text{min}$ and peak temperatures were 1200° and 1600°C . Both alumina and platinum-type crucibles were used.

3.2.3.4 X-Ray Diffraction Study

Calcined powders were analyzed for phases present using X-ray diffraction on either a Sintag or a General Electric diffractometer.

X-ray densities were calculated from d-spacing measurements on the Sintag. The Sintag was calibrated in the relevant d-spacing range using a silicon wafer.

The solubility of CaCrO_4 in $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$ was also studied by X-ray diffraction using the Sintag. Disk specimens for $x = 0.1$, 0.2 , and 0.3 were sintered for 2 hr at temperatures of 1100° , 1200° , 1300° , 1400° , and 1500°C . More work is being done to determine the solubility limits. In addition, solubility data for compositions ranging from $x = 0.35$ to 0.60 are presently being accumulated.

An additional experiment was performed on powder and disk specimens of $\text{La}_{0.99-x}\text{Ca}_x\text{CrO}_3$, $x = 0.3$ and 0.4 to see if CaCrO_4 would segregate at temperatures at which the solubility limit of Ca in LaCrO_3 was exceeded. The disks and powders were heated to 970°C for 4 hr and analyzed by X-ray diffraction to ensure the presence of CaCrO_4 . Powder and pellets were then heated to 1500°C for 2 hr to dissolve the CaCrO_4 into the matrix and again analyzed for the phases present. Finally, the specimens were annealed at 850°C for 100 hr and analyzed for phases present.

3.2.3.5 Depth Profiles on $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$

Auger electron spectroscopy (AES) depth analysis was conducted on compacted powders and sintered pellets of $\text{La}_{.89}\text{Ca}_{.1}\text{CrO}_3$. The powders were uniaxially pressed to 70 MPa after calcination at 800°C for 8 hr. The sintered pellets were prepared by isostatically pressing the powders to 210 MPa after calcination at 400°C. Sintering was carried out at 1500°C for 2 hr.

The AES instrument had a sputtering area of about 10 mm² and electron beam area of about 3 mm². Sensitivities for each element were back-calculated from bulk measurements. As a consequence of analyzing rough surfaces, only a qualitative estimate of the sputter depths could be obtained. This was acceptable as a first approximation, however, a microprobe technique that is able to analyze a smaller area must be used in future experiments to clearly define the depth profile of an individual particle.

3.2.3.6 $\text{La}_{.69}\text{Cr}_{.3}\text{O}_3$ / Ca-Cr-O Reaction Study

Powders of the compositions CaCrO_4 , $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$, $\text{Ca}_3\text{Cr}_2\text{O}_8$ and CaCO_3 were prepared as above. The calcination temperatures varied between 400° and 800°C to avoid melting. As a result, the $\text{Ca}_3\text{Cr}_2\text{O}_8$ composition consisted of a CaO-CaCrO_4 mixture rather than the pure $\text{Ca}_3(\text{CrO}_4)_2$ phase. Hence, the notation $\text{Ca}_3\text{Cr}_2\text{O}_8$ is used. The effect of using this as opposed to single-phase $\text{Ca}_3(\text{CrO}_4)_2$ will be shown later.

To observe the melting characteristics of the four Ca-Cr-O compositions, 1.2-cm-dia disks were pressed from each composition and placed on 2.5-cm-dia disks of $\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_3$ and $\text{La}_{.675}\text{Ca}_{.3}\text{CrO}_3$. The reaction couples were then heated to 1100°C and in a separate run to 1230°C, held for 2 hr and furnace-cooled. Later, 1.2-cm disks of $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and $\text{Ca}_3\text{Cr}_2\text{O}_8$ were placed on 2.5-cm disks of CaCO_3 , heated to 1230°C and furnace-cooled.

3.2.3.7 Nonstoichiometric Mixtures

A nonstoichiometric compound, $\text{La}_{.675}\text{Ca}_{.3}\text{CrO}_3$, was prepared using the modified Pechini technique described above. It was calcined at 800°C for 8 hr and mixed with each of the powders: CaCO_3 , $\text{Ca}_3\text{Cr}_2\text{O}_8$ and $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ in reagent grade methyl alcohol. After milling, the powders were dried, and isostatically pressed into 1.2-cm disks at 210 MPa. Two disks of each composition were then sintered at 1020°C for 2 hr and at 1400°C for 1 hr. The following reactions were used to estimate the stoichiometry of the final products:

3.2.3.8 Discussion

3.2.3.8.1 Phase Relations

Two phases appear when lanthanum chromite powders ($x > 20$ percent Ca) made from the Pechini method are calcined at 800°C for 8 hr. Calcium chromate (CaCrO_4) and a lanthanum calcium chromate solid solution ($\text{La}_{.99-x}\text{Ca}_x\text{CrO}_4$) first appear at the burnout of carbon and crystallization of the char above 400°C . Thermal analysis shows the transformation of lanthanum chromate to lanthanum chromite between 700° and 800°C is apparent from the large endothermic peak shown in Figure 3-18. This peak shifts to lower temperatures as the Ca content increases. The DTA also shows that a liquid phase forms in all the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ composition at approximately 1030° to 1080°C .

Figure 3-18. DTA Runs of $\text{La}_{.79}\text{Ca}_{.2}\text{CrO}_3$ (LCC-20), $\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_3$ (LCC-30) and $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ (LCC-40) in Pt. Heating Ramp Rate $10^{\circ}\text{C}/\text{min}$

By comparing Figure 3-18 and the $\text{CaO}-\text{Cr}_2\text{O}_3$ phase diagram,⁽²⁾ shown in Figure 3-19, it became evident that the liquid phase formed at $\sim 1030^{\circ}\text{C}$ in the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3/\text{CaCrO}_4$ mixture was actually the eutectic associated with the CaCrO_4 phase. However, CaCrO_4 melts incongruently forming a eutectic liquid, $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4.8}$ and a higher melting point solid, CaCr_2O_4 . This indicated that CaCrO_4 is ineffective as a sintering aid for $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$.

Figure 3-19. Equilibrium Phase Diagram for the CaO-Cr₂O₃ System, After Ford and White⁽²⁾

3.2.3.8.2 Reaction Mechanism

Using this information, and the results from Auger spectroscopy, X-ray diffraction, and from SEM analysis, a reaction mechanism is proposed which explains the sintering behavior up to and including the solubility temperature of CaCrO_4 in these powders. Figure 3-20 illustrates the mechanism.

When the powders are calcined below the solubility limit, CaCrO_4 appears in X-ray patterns of $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$. However, at this stage, SEM micrographs do not seem to show the presence of distinct CaCrO_4 crystallites. This might be further studied with back-scatter techniques in subsequent SEM analyses.

The Auger results suggest the formation of a calcium-rich layer upon initial sputtering of the powders (Figures 3-21 and 3-22). This gives evidence of the CaCrO_4 coating proposed in the first step of the mechanism. At $\sim 1030^\circ\text{C}$, incongruent melting occurs. The liquid formed is very reactive towards the excess chromium in the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ as is later discussed in the reaction studies section. It is tentatively believed that calcium in the liquid at the coating/particle interface is absorbed, leaving behind a composition which acts as a barrier to lanthanum transport.

Particle rearrangement also takes place in this temperature range which suggests that there is liquid present at particle contact points.

Although not shown in the model, it becomes apparent that the Ca-Cr-O phase also begins to segregate from the $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ (into large masses), as shown in the SEM photomicrograph of Figure 3-23, for a quenched $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ specimen. The specimen was heated at 1400°C for 3 min and was air-quenched. It appears that the dendritic CaCrO_4 structure has segregated from the $\text{La}_{.59+\delta}\text{Ca}_{.4-\delta}\text{CrO}_3$ matrix. Elemental analysis using EDS shows no measurable amount of lanthanum within the CaCrO_4 . Mixtures of CaCrO_4 and lanthanum carbonate are presently being made to further study the solubility of lanthanum in CaCrO_4 .

At higher temperatures (now being determined for each composition) the CaCrO_4 completely dissolves into the matrix. This became evident when all the compositions containing CaCrO_4 second phase (up to 40-percent calcium) were X-rayed after sintering at 1500°C . In addition, the CaCrO_4 was observed to reappear after the pellets had been annealed at 800°C for 100 hr, suggesting that these reactions are reversible.

3.2.3.8.3 Reaction Studies

The reaction studies, although providing only qualitative results, give more insight to the reactions of the Ca-Cr-O compositions with $\text{La}_u\text{Ca}_v\text{CrO}_3$ or other substrates. It was observed that when a CaCrO_4 disk was heated on either alumina or platinum substrates, to temperatures as high as 1500°C , a liquid exsolved out and spread over the substrate leaving a porous skeleton of the disk. However, at 1030°C , $\text{Ca}_{1.09}\text{Cr}_{.91}\text{O}_{4-\delta}$ melted completely in a platinum TG/DTA crucible but not in alumina. Interactions between Ca-Cr-O compositions and various substrates were then studied.

Particles after calcining at 800°C are coated with CaCrO_4 .

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Figure 3-20. Proposed Sintering Mechanism for The $\text{La}_{.99-x}\text{Ca}_x\text{CrO}_3$ System

Figure 3-21. Auger Analysis of Pressed Pellet of $\text{La}_{0.69}\text{Ca}_{0.30}\text{CrO}_3$

Figure 3-22. Auger Analysis of Sintered Surface of $\text{La}_{0.69}\text{Ca}_{0.30}\text{CrO}_3$

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Figure 3-23. A SEM Micrograph of $\text{La}_{0.59}\text{Ca}_{0.4}\text{CrO}_3$ Air-Quenched from 1400°C

The first experiment consisted of 1.2-cm disks of CaCrO_4 , $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$, $\text{Ca}_3\text{Cr}_2\text{O}_8$ and CaCO_3 , on 2.5-cm disks of $\text{La}_{0.69}\text{Ca}_{0.3}\text{CrO}_3$. After heating at 1100°C for 2 hr, the CaCrO_4 retained its size and shape, but had lost liquid into the $\text{La}_{0.69}\text{Ca}_{0.3}\text{CrO}_3$ and had the characteristic porous, skeletal appearance. The $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ had contracted, deformed, and liquified at the interface with the substrate. The $\text{Ca}_3\text{Cr}_2\text{O}_8$ remained unchanged in size and shape but changed from a bright yellow ($\text{CaO} + \text{CaCrO}_4$) to a dark green color (perhaps formation of $\text{Ca}_3(\text{CrO}_4)_2$). No evidence of melting could be seen, however the CaCO_3 pellet transformed into unsintered CaO .

The main contrast between the 1100°C and the 1230°C run is that at 1230°C , the $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ had completely melted into the substrate and the $\text{Ca}_3\text{Cr}_2\text{O}_8$ had clearly melted, contracted, and densified areas of the $\text{La}_{0.69}\text{Ca}_{0.3}\text{CrO}_3$ substrate beneath it.

When the same Ca-Cr-O pellets were set on $\text{La}_{0.675}\text{Ca}_{0.3}\text{CrO}_3$ substrates and heated to 1230°C for 2 hr, the $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and the $\text{Ca}_3\text{Cr}_2\text{O}_8$ experienced poor melting. Although this experiment needs to be repeated, it seems to indicate that the Ca-Cr-O compositions have a greater difficulty melting in the presence of excess chromium. As in the case of the alumina setters, the calcium in the system may be leached out preferentially, leaving an unreacted solid.

To prove this, $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and $\text{Ca}_3\text{Cr}_2\text{O}_8$ pellets were set on CaCO_3 disks and heated them to 1230°C . At about 1030°C , the $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ began to melt and spread over the surface of the substrate forming a clear sessile drop. The $\text{Ca}_3\text{Cr}_2\text{O}_8$

also began to melt near 1230°C. It soaked into the CaO substrate and the pellet on top quit melting only after the liquid had soaked the zirconia setter beneath the CaO. Apparently, the liquid phase is very reactive to solids which will readily dissolve calcium ions such as, alumina, zirconia, and chromium excess lanthanum chromite.

3.2.3.9 Nonstoichiometric Mixtures

It was suggested that mixing a calcium-rich, congruent melting powder of Ca-Cr-O with chromium excess $\text{La}_u\text{Ca}_v\text{CrO}_3$ ($u+v < 1$) would cause reaction liquid phase sintering to occur. The composition of the mixture would be such that it ultimately formed a stoichiometric product.

Compositions based on the three chemical equations (1), (2), and (3) were prepared. The eutectic composition $\text{Ca}_{1.09}\text{Cr}_{0.91}\text{O}_{4.8}$ and $\text{Ca}_3(\text{CrO}_4)_2$ qualified as congruent melting liquid phases. Calcium carbonate served as a control end member. Disks of the mixtures from equations (1) and (2) were first heated to 1020°C for 2 hr and then heated to 1400°C and annealed for 1 hr. An identical heating schedule was used later for mixtures of equation (3).

The mixture from equation (2) sintered to 90 percent of full density whereas the other compositions showed little improvement over the conventional compositions. SEM micrographs of the fractured specimen are shown in Figures 3-24 and 3-25. Figure 3-24 shows well-sintered grains that have grown as large as 5 microns. Figure 3-25 is a back-scatter photo that shows the chemical homogeneity. Although the calculated reaction results in a lanthanum-rich product, the ceramic appears to be chemically homogeneous.

3.2.3.10 Conclusions

According to German³, the solubility of the liquid phase in the solid must be low and the solubility of the solid in the liquid must be high for optimum liquid phase sintering. Many of our results show just the opposite. This may be a result of exceeding the optimum heating ranges. Continuing work will center on determining the solubility limits of CaCrO_4 in LaCrO_3 and La in CaCrO_4 . From this work, optimum densification of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$ may be identified by determining the temperature region of low liquid and high solid solubility for a given composition.

3.2.4 Liquid Phase Sintering of $(\text{La,Ca})\text{CrO}_3$

Recent work has focused on improving processing techniques to gain uniform green microstructures, in addition to compiling results on the low temperature reactions (400° to 1300°C) in the calcium doped lanthanum chromium oxide system.

The liquid mix technique used to prepare previous compositions resulted in powders composed of irregular shaped aggregates as large as 50 μm and a nonuniform size distribution. Green compacts fabricated by uniaxial and isostatic pressing showed poorly packed microstructures. Such a green state was previously ignored since liquid phase sintering is typically accompanied by particle rearrangement which improves the packing density. In our system, this mechanism was observed as large agglomerates

Figure 3-24. SEM Micrograph of Sintered $\text{La}_{0.618}\text{Ca}_{0.4}\text{CrO}_3$ (Calculated Composition). Heated at 1020°C/2 Hr and 1400°C/ Hr

Figure 3-25. Sintered $\text{La}_{0.618}\text{Ca}_{0.4}\text{CrO}_3$. SEM Elemental Back-Scatter Image

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composed of 0.1 μm crystallites rearranged into a compact with greater packing efficiency. However, this process was not as efficient as hoped and large pores were preserved in the microstructure at the completion of sintering.

The intention was to improve the powder processing and consolidation steps and obtain a better green microstructure, to gain a better perspective on the mechanism of sintering. A milling study on char particles was performed since these particles were thought to break down easier than the aggregates obtained after calcination. A low temperature calcination in neutral atmosphere was used to control carbon burn-out as well as to obtain the lanthanum chromate (LaCrO_4) intermediate phase. A consolidation technique using colloidal dispersions is presently being employed to acquire a uniformly packed green state.

In addition to improvements on the powder processing and consolidation stages, results on the study of reactions occurring within the 400° to 1300°C temperature range are presently being concluded.

The LaCrO_4 intermediate phase was studied because of the high solubility of calcium in its crystal structure. The consolidation of powders using colloidal dispersions is achieved easier when only a single phase material is dispersed. In addition, the formation CaCrO_4 upon the transformation of LaCrO_4 to LaCrO_3 , will more likely be evenly distributed in a compact than if it were allowed to precipitate and grow during powder calcination.

The liquid phase formation in calcium doped lanthanum chromite is found to be a result of the incongruent melting of CaCrO_4 . The properties of the liquid are related to the $\text{CaO-Cr}_2\text{O}_3$ phase system.

A solubility diagram has been constructed to illustrate the solubility of CaCrO_4 in LaCrO_3 vs temperature. This diagram is helpful in determining optimum calcium additions and sintering temperatures.

Binary mixtures of powders are presently being prepared and studied to increase the volume percent of liquid phase. Previous work involved milling fully calcined (800°C for 8 hr) non-stoichiometric compositions together to ultimately obtain stoichiometric products. Equation (4) is an example of one of the mechanical mixtures prepared.

The emphasis on the present work with binary powder mixtures is to obtain better a green microstructure using the colloidal dispersion technique.

3.2.4.1 Experimental Procedure

3.2.4.1.1 Powder Processing

Powders were prepared based on the modified resin process proposed by Tai *et al.* (NO TAG) Metal nitrates or carbonates were dissolved into water and nitric acid and the solution was combined with an ethylene glycol/citric acid mixture having a mole ratio of

1:1:1. The solution was heated to drive off water and nitrates, and allowed to form a gel. The gel was then poured into large, shallow, ceramic dishes in a pre-heated drying oven at approximately 120°C. The gel boiled rapidly in the pan and charred. Unlike the previous method of charring in tall beakers, this technique obtained better combustion of the polymer, producing a fluffy, gray colored ash.

3.2.4.1.2 Milling Study

A milling study was performed to determine the advantage of milling the char before calcination. Char, having the final composition $\text{La}_{.89}\text{Ca}_{.1}\text{CrO}_3$, was milled in reagent grade ethyl alcohol using a Sweco vibratory mill for 2, 4, 6, and 8 hr. Microanalysis of the milled char particles was performed on a scanning electron microscope and particle size was determined using a sedigraph-type particle size analyzer.

3.2.4.1.3 Lanthanum Chromate

The formation of the monoclinic LaCrO_4 phase was accomplished by slowly heating milled char under a flowing argon atmosphere to 550°C and held for 8 hr. The char was also spread in a thin layer along a large MgO tube to ensure uniform heating.

3.2.4.1.4 Powder Classification and Consolidation

A powder classification and consolidation technique for lanthanum chromite was previously developed by Jang.^(NO TAG) His general procedure is as follows. Single-phase calcium doped lanthanum chromate powder is heated to 400°C for 2 hr to drive off surface water. The powder is then removed from the hot furnace and cooled in a desiccator. Methyl ethyl ketone is mixed with an optimum percentage of Menhaden fish oil in a beaker. The cooled powder is then mixed in this solution using an ultrasonic probe. The dispersion is allowed to sit for a predetermined time to allow the settling of large aggregates. The dispersion is then poured off into a tube and centrifuged, to form a compact of the dispersed powders. The clear solution is then poured off and saved for future use for similar powders. The resulting compact is then dried to a green state.

Binary mixtures of lanthanum chromite and liquid phase powders will be prepared in a similar manner as described above with the exception that single phase powders will be dispersed and classified in separate containers and then mixed together before forming the green compact in the centrifuge.

3.2.4.1.5 Liquid Phase Characteristics

The formation of the liquid phase within calcium doped lanthanum chromite was analyzed by using SEM and energy dispersive analysis (EDS) on quenched specimens. Melting and freezing points were determined using differential thermal analysis (DTA). X-ray diffraction studies were also performed to analyze lanthanum solubility within CaCrO_4 . Characteristics of the liquid were studied by placing pellets of composition $\text{Ca}_3\text{Cr}_2\text{O}_8$, $\text{Ca}_{1.2}\text{CrO}_4$ and CaCrO_4 on various substrates and heating beyond their melting points and observing the melting behavior.

3.2.4.1.6 Solubility of CaCrO_4 in LaCrO_3

To determine the solubility of CaCrO_4 in LaCrO_3 , uniaxially compacted pellets of calcined $(\text{La,Ca})\text{CrO}_3$ containing exsolved CaCrO_4 , $20\% \leq \text{Ca} \leq 65\%$ were heated in air between 900°C and 1450°C for 12 hr and air quenched. The specimens were then polished to remove surface effects. Phase analysis was performed using X-ray diffraction.

3.2.4.2 Discussion

3.2.4.2.1 Powder Processing

Powders made by the liquid mix (Pechini) process and calcined above 800°C have crystallite sizes of about $0.1\ \mu\text{m}$ which are typically fused together into aggregates as large as $50\ \mu\text{m}$. Microanalysis shows that the final aggregate size and shape is dictated by size and shape of the char particles. Char particles are amorphous according to X-ray diffraction and in the SEM have the appearance of an organic residue. Since the char particles are relatively soft, it was believed to be advantageous to mill the powders before calcination.

Micrographs (Figures 3-26 and 3-27) of the milled char indicate a particle size reduction from as large as $50\ \mu\text{m}$ for "as is" powder to less than $2\ \mu\text{m}$ after milling for 8 hr. Figure 3-28 illustrates the particle size distribution of powders milled for 8 hr and calcined at 550°C in Argon.

3.2.4.2.2 LaCrO_4 Phase

Lanthanum chromate (LaCrO_4), is a low temperature phase which is stable below 650°C . This compound has two polymorphs, tetragonal $14_1/\text{amd}$ (141) and monoclinic, $\text{P}2_1/\text{n}$ (14). Monoclinic LaCrO_4 is formed in powders upon the burn-out of organics. X-ray diffraction of the above calcined powder indicates that lanthanum chromate forms a solid solution with calcium chromate, allowing substitutions as high as 40 percent.

Thermal analysis indicates the chromate phase loses oxygen and transforms to orthorhombic lanthanum chromite above 650°C . It is shown in Table 3-12 that this transition temperature is dependent on the amount of calcium within the system. Although this effect is not completely understood, it gives further evidence that calcium is incorporated within the LaCrO_4 lattice, forming a solid solution.

There has previously been difficulty in forming the pure LaCrO_4 phase. Since residual organics were retained within the char, the burn-out process was difficult to control as a result of combustion heating. Hence, the temperature often increased above the lanthanum chromate to lanthanum chromite transition within the interior of the mound of powder. This resulted in a partial, and sometimes a complete transition to the lanthanum chromite phase.

Figure 3-26. LaCrO_x Char Particles

Figure 3-27. LaCrO_x Char Particles, Milled 8 Hr

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Figure 3-28. Particle Size Distribution of $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_4$,
Calcined $550^\circ\text{C}/8\text{Hr}/\text{Argon}$

TABLE 3-12	
THE EFFECT OF CALCIUM ADDITIONS ON THE $\text{LaCrO}_4 \rightarrow \text{LaCrO}_3$ TRANSITION TEMPERATURE	
Composition	Transition Temperature
$\text{La}_{.89}\text{Ca}_{.1}\text{CrO}_4$	$\sim 770^\circ\text{C}$
$\text{La}_{.79}\text{Ca}_{.2}\text{CrO}_4$	710°C
$\text{La}_{.69}\text{Ca}_{.3}\text{CrO}_4$	705°C
$\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_4$	655°C

The carbon burn-out reaction was prolonged by slowly heating the char under an argon atmosphere to 550°C and holding for 8 hr. Thermogravimetric analysis under the same heating rate, temperature and hold time shows a gradual weight loss which eventually stabilizes, an indication that most of the organic material was burned off.

3.2.4.2.3 Liquid Phase Characterization

The liquid phase formed in the $(\text{La,Ca})\text{CrO}_3$ system, was found to be the result of the incongruent melting of CaCrO_4 . This phase exsolves at the transition of LaCrO_4 to

LaCrO_3 when calcium substitutions exceed 10 percent and calcination temperatures range from 800°C to 1200°C . Figure 3-29 is a comparison of the melting and freezing peaks of $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ (LCC-40) with that of the Ca-Cr-O eutectic composition ($\text{Ca}_{1.2}\text{CrO}_4$). The sharpness of the melting peak of $\text{Ca}_{1.2}\text{CrO}_4$ is an indication of a congruently melting liquid. Conversely, the wide shallow melting peak of LCC-40 indicates an incongruently melting liquid. In addition, the matching onset temperatures of the melting and freezing peaks in $\text{Ca}_{1.2}\text{CrO}_4$ are an indication of a single melting point.

The eutectic liquid is highly mobile and unstable. It spreads and wets adjoining porous solids (such as setter plates), especially those with a high calcium solubility. Calcium then diffuses from the liquid into the solid leaving a solid residue. Figures 3-30 and 3-31 show the results of the reaction studies of various Ca-Cr-O compounds set on porous $\text{La}_0\text{Ca}_v\text{CrO}_3$ pellets.

Figure 3-29. DTA Melting and Freezing Peaks of $\text{Ca}_{1.2}\text{CrO}_4$ and $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ Liquid-Phase

The CaCrO_4 pellets in each case formed a small amount of liquid which was drawn into the porous substrate, leaving behind a skeleton of unreactive solid. Evidence of densification in the $\text{La}_u\text{Ca}_v\text{CrO}_3$ showed immediately below the CaCrO_4 pellet.

The eutectic, $\text{Ca}_{1.2}\text{CrO}_4$ as well as the calcium rich specimens, $\text{Ca}_3(\text{CrO}_4)_2$ are seen to dissolve less readily into the substrates which have a greater chromium excess. The shape of the top pellets also indicate that less efficient melting occurred on these substrates. This is an indication of reactivity of the calcium within the liquid phase. Calcium diffuses out of the eutectic liquid when in contact with a solid having a high solubility for calcium, leaving behind an unreactive solid. Other reaction studies with $\text{Ca}_{1.2}\text{CrO}_4$ and $\text{Ca}_3(\text{CrO}_4)_2$ on Pt and CaCO_3 showed complete melting. In these cases, the calcium remained within the liquid, allowing it to melt completely.

The eutectic liquid also appears to have a low solubility for other metal cations. Qualitative EDS analysis of the liquid phase in $\text{La}_{.59}\text{Ca}_{.4}\text{CrO}_3$ contained no measurable amount of lanthanum. In addition, a solubility experiment was performed in which 2 and 5% La_2O_3 was mixed and reacted with CaCrO_4 . X-ray diffraction analysis indicated the formation of LaCrO_3 . Further work needs to be done to better understand this portion of the LaCrO_3 - CaCrO_4 solubility diagram.

3.2.4.2.4 Solubility Diagram

The Ca-Cr-O eutectic liquid reabsorbs into the perovskite lattice at temperatures dependent on the calcium composition. Figure 3-32 is a solubility diagram showing progress on this study. Solubility temperatures will ultimately be determined by following lattice parameter changes as a function of temperature. One difficulty in obtaining this diagram is the recent discovery that the orthorhombic-rhombohedral transition in LaCrO_3 has an effect on the solubility of CaCrO_4 . Apparently, the high temperature rhombohedral structure has a lower solubility than does room temperature orthorhombic.

3.2.4.2.5 Binary Powder Mixtures

Binary powder mixtures of $\text{La}_u\text{Ca}_v\text{CrO}_3$ and $\text{Ca}_n\text{Cr}_m\text{O}_4$ have shown promise in obtaining dense lanthanum chromite. The composition obtained 90-percent theoretical density.

3.2.5 Interconnect Studies at AlliedSignal

This effort focused mainly on the cofiring of the interconnect laminated with the other cell components. Emphasis was placed on the effect of the lamination on interconnect densification. In addition, effects of interconnect powder characteristics were investigated. Tapes were prepared with lanthanum chromite powders treated in a variety of ways. The tapes were evaluated to determine any processing or powder preparation conditions that could influence densification.

Tapes were initially prepared using the as-received powder (surface area = $2.91 \text{ m}^2/\text{g}$) and powder that was ball-milled and calcined (surface area = 1 to $2 \text{ m}^2/\text{g}$). The measured surface area is average surface area for spherical agglomerates of the

1230°C 2hr

CaCrO_4 on $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_{1.2}\text{CrO}_4$ on $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_3(\text{CrO}_4)_2$ on $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$

Figure 3-30. Reaction Couples, $\text{La}_{.675}\text{Ca}_3\text{CrO}_3$ Substrate

1230°C 2hr

CaCrO_4 on $\text{La}_{.69}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_{1.2}\text{CrO}_4$ on $\text{La}_{.69}\text{Ca}_3\text{CrO}_3$

$\text{Ca}_3(\text{CrO}_4)_2$ on $\text{La}_{.69}\text{Ca}_3\text{CrO}_3$

Figure 3-31. Reaction Couples, $\text{La}_{.69}\text{Ca}_3\text{CrO}_3$ Substrate

F-66164

B-27022

Figure 3-32. The Solubility of CaCrO_4 in LaCrO_3 vs Temperature

lanthanum chromite. In most cases, the as-received powder when mixed with the binder and plasticizer could not be rolled into a tape. Tapes made of lanthanum chromite, which was milled and calcined, could easily be made into tapes; however, only a maximum density of 94-percent theoretical density was achieved by sintering at 1400°C for 1 hr. The as-sintered and fractured surfaces of this material, shown in Figure 3-33, indicate that there is a lot of enclosed porosity residing at the grain boundaries.

The tape composed of the as-received powder that would not roll was heated to remove the binder so that the powder could be used in subsequent batches. The powder had a surface area of 18.5 m²/gm after it was debindered. The high surface area indicated that the soft agglomerates were broken down during shear mixing when the plastic mass was being formed. This powder was calcined at temperatures above 1000°C for 5 hr and then made into tapes. Sintering of this tape resulted in densities of 94-percent theoretical density, similar to those of the previously prepared material (ball-milled and calcined). The as-sintered surface of this material, shown in Figure 3-34, is more uniform and shows very little porosity in the microstructure. The fracture surface shows a similar distribution in the amount of porosity in the microstructure as compared to the sample shown in Figure 3-33; however, the size of the porosity is much larger in the sample in Figure 3-34.

This result indicates that the as-sintered microstructure can be improved by breaking down the agglomerates in the as-received powder into their individual particles. There is no change, however, in the sintered density of the material.

The interconnect work centered on fabricating and processing A/I, C/I, CE/I, and A/I/CE tapes, bonding them to anode and intermediate corrugations, and evaluating sintering and densification of the bonded structures. The interconnect material used in this work had the composition La_{0.84}Ca_{0.2}Cr_{0.9}Co_{0.1}O₃. The anode, cathode, and intermediate tapes used were standard baseline batches. All bilayers and trilayers used in this study were fabricated such that the thickness of the anode and cathode were no greater than 12 μ.

Initially, A/I bilayers were bonded to anode corrugations and C/I and CE/I bilayers were bonded to CE corrugations. Figure 3-35A shows a SEM micrograph of the fracture surface of an A/I bilayer bonded to an anode corrugation. Good bonding was observed between the bilayer and the corrugation. Figure 3-35B shows a lower magnification of the sample shown in Figure 3-35A. In Figure 3-35B, two areas are identified A and B, and high magnification micrographs of these areas are shown in Figures 3-36 and 3-37. In Figure 3-36, the A series of micrographs shows the interconnect at position A of Figure 3-35B. It can be seen from these photographs that both the grain size and density of the material increased as the distance increased from the bond site. Figure 3-37 shows the same progression at area B of Figure 3-35B. In this series of micrographs, the density does not appear to change; however, the grain size increases dramatically as distance increases from the anode. Additional studies by EDS have indicated that the inhibition of grain growth near the anode is due to ZrO₂ diffusing out of the anode and into the interconnect.

As-Sintered

Fracture

F-64414

Figure 3-33. As-Sintered and Fracture Surfaces of Lanthanum Chromite Sintered 1400°C for 1 hr. Powder from Lot 0260, Ball-Milled and Calcined

As-Sintered

Fracture

F-64415

Figure 3-34. As-Sintered and Fracture Surfaces of Lanthanum Chromite Sintered 1400°C for 1 hr. Powder from Lot 0260, Previously Made into Tape in As-Received State

Figure 3-35. SEM Micrographs Showing Fracture Surface of A/I Bilayer Bonded to A Corrugation

Figure 3-36. SEM Micrographs of Interconnect at Increasing Distance from A/I:A Bond

F-65887

Figure 3-37. SEM Micrographs of Interconnect at Increasing Distance from Anode.

A similar study was carried out for CE/I and C/I bilayers bonded to CE corrugations. Figure 3-38 shows the SEM micrographs of the fracture surface of a C/I bilayer bonded to a CE corrugation. The bonding of the C/I to the CE corrugation looks very good. Figures 3-39 and 3-40 show the change in microstructure at the points indicated A and B in Figure 3-38B. Figure 3-39 shows the fracture surfaces of the interconnect at increasing distances below the bond site. This series of micrographs shows a dramatic change in grain size and density as the distance from the bond increases. Figure 3-40 shows the fracture surfaces of the interconnect at various distances from the cathode layer, at position B. In this series of micrographs there was little or no change observed in the microstructure or density of the interconnect.

Polished cross sections of the bonded materials were evaluated to determine porosity levels in the interconnect. Figure 3-41 shows an optical micrograph of a polished cross section of an A/I bilayer bonded to an A corrugation. The interconnect in the local area of the bond site is porous and very dense in areas not bonded to the anode corrugation. The incomplete densification of the interconnect is due to the liquid chromate phases being drawn out of the interconnect by the porous anode. Figure 3-42 shows high magnification optical micrographs of C/I and CE/I bilayers bonded to CE corrugations. In Figure 3-42A, CE/I bonded to CE, the interconnect has a layer of porosity adjacent to the CE layer. Also, the porosity in the interconnect appears to be uniform across the thickness of the interconnect. In Figure 3-42B, C/I bonded to CE, there is a larger amount of porosity adjacent to the bond site which decreases rapidly, corresponding to the micrographs shown in Figure 3-39. From the SEM and optical micrographs, it appears that the interconnect densifies better when it is adjacent to unmodified cathode material. The cracks observed in the samples resulted from the mounting and polishing steps.

The work with the C/I and CE/I bilayers was extended to trilayers. Two types of trilayer were fabricated, one being A/I/CE and the other an A/I/C. Both tapes were bonded to CE corrugations and sintered. The optical micrographs of the polished cross sections, shown in Figure 3-43, verify that the trilayer fabricated with an unmodified cathode layer (C) densifies much better than one with the modified cathode (CE). Again, the cracks observed in the polished samples resulted from the mounting and polishing of the sample.

Sintering studies were carried out to determine if the bilayer and trilayer could be bonded to single-cell modules and sintered successfully. Modules prepared with baseline materials were obtained and bonded to A/I, C/I, or A/I/C tapes on one side of the module. Samples were sintered at 1400° and 1350°C for 1 hr. In most cases when modules bonded with an A/I flat plate were sintered, they came out flat and crack-free. However, when modules were sintered with C/I flat plates, the modules fractured across the CE corrugation. In the case of an A/I/C trilayer flat plate bonded to the anode side of the module, the module showed warping towards the CE corrugation. When the trilayer was bonded to the CE corrugation, the sintered module fractured across the CE corrugation.

The work thus far was carried out using interconnect tapes with a solids loading of 50-vol percent. Interconnects with a lower solids loading were investigated in an

F-65877

Figure 3-38. SEM Micrographs Showing Fracture Surface of C/E Bilayer Bonded to CE Corrugation

F-65886

Figure 3-39. SEM Micrographs of Fracture Surfaces Showing Changes in the Interconnect at Various Distance from the C/I:CE Bond

F-65885

Figure 3-40. SEM Micrographs of Fracture Surfaces Showing Interconnect Microstructure at Various Distances from Cathode

F-65878 -A

Figure 3-41. Optical Micrograph of a Polished Cross Section of A/I Bonded to an Anode Corrugation Showing Porosity (Gray Area) by Bond Region

attempt to reduce the observed warping and fracture when the bilayer and trilayers were bonded to the modules. Thus, the above mentioned studies were repeated using an interconnect tape fabricated with a 47-vol% solids loading. The results, however, showed no improvement.

In other experiments the main variable evaluated was the thickness ratio of the anode or cathode and interconnect layers. Bilayers were fabricated with decreasing electrode-to-interconnect thickness ratio, i.e., the electrode thickness decreased (interconnect thickness increased) while the overall thickness of the tape remained constant (about 10 to 11 mils or 255 to 280 μ). Figure 3-44 shows the progression of decreasing anode thickness and its effect on the densification of the interconnect in the A/I bilayer. It was observed that when the anode thickness was less than 15 μ both the anode and interconnect became fully dense when sintered at 1400°C for 1 hr. Figure 3-45 shows the same progression for CE/I bilayers. Again, both the CE and interconnect became fully dense when the CE thickness was less than 15 μ .

It appears that in these thin anode and cathode layers, the electrode pore volume fills with chromate liquid phases from the interconnect during firing and densifies, thus allowing the interconnect to also fully densify. In the thicker electrode layers, however, the pore volume greatly exceeds the volume of liquid generated and acts as a sink for the liquid, preventing both layers from densifying.

Trilayers were fabricated with thin anode and cathode layers. The A/I/CE trilayers were sintered at 1400°C for 1 hr. Figure 3-46 shows a fracture surface of such a

Figure 3-42. Optical Micrographs of Polished Cross Sections of (A) CE/I on CE and (B) C/E on CE Showing Porosity in Interconnect

Figure 3-43. Micrographs of A/I/CE and A/I/C Bonded to CE Corrugations

F-66166

Figure 3-44. SEM Photographs of Anode/Interconnect Bilayers Showing Influence of Layer Thickness on Interconnect Densification

Figure 3-45. SEM Photographs of Cathode/Interconnect Bilayer Showing Influence of Layer Thickness on Interconnect Densification

F-66167

F-66165

Figure 3-46. Fracture Surface of A/I/CE Trilayer Showing Densification of Anode, Interconnect, and Cathode Layers (1400°C for 1 hr)

trilayer. Several distinct features were observed for the sintered trilayers: (1) the interconnect is fully dense, (2) the anode cannot be visually distinguished from the interconnect, and (3) the CE/I interface is slightly porous and has a finer grain size.

Elemental line scans (40 equidistant points) were carried out on polished cross sections of the A/I/CE trilayer to determine the diffusion profiles of the various elements. A typical scan of Ca, Co, La, and Cr is shown in Figure 3-47. From this analysis, cobalt was observed to be uniformly distributed across all three layers as was chromium in the anode and interconnect. There was a higher concentration of calcium in the cathode than anywhere else. X-ray diffraction was used to identify compounds present in the anode layer. Figure 3-48 shows the diffraction pattern taken from the anode surface. This figure shows that the phases present are LaCrO_3 and CaZrO_3 and trace amounts of NiO and ZrO_2 .

3.3 STUDY OF LONG-TERM CATHODE STABILITY

The objectives of this task were to determine the effect of long-term operation of the MSOFC on the cathode performance and to develop a unified theory of interfacial and bulk phenomena in the fuel cell. Densification, manganese migration, and other physical and chemical changes of the cathode may be a problem in long-term fuel cell operation. Determining and understanding the mechanisms of interfacial reactions and degradations will allow the cathode to be modified to improve its overall performance.

3.3.1 Long-Term Effects of Operation of the Cathode

Platinum paste screen current collectors were applied to a series of symmetric CE/E/CE (SC 1193) composites. Four composite samples, two with current collectors and two without, were placed in each of three furnaces. The three furnaces were brought up to operating temperatures of 1000°, 1100°, and 1200°C. The electrochemical performance of the composites in air at each of the three temperatures was monitored using an established ac impedance technique.

The area specific resistance, over the 1000-hr study, of the CE/E/CE composites' cathode/electrolyte interfaces at 1000°, 1100°, 1200°C are given in Figures 3-49, 3-50, and 3-51, respectively. The figures also show the times at which the samples were removed from the furnace for posttest examination. Generally, the interfacial resistance of the composites at 1000°C increased slightly, while the 1100°C data exhibited a clear upward trend, and the 1200°C results showed the greatest increase. While the 1000°C results were relatively linear, the slope of the 1100° and 1200°C data decreased with time, with the decrease in slope being more dramatic in the 1200°C data.

Posttest examination of the CE/E/CE composites after the 1000-hr tests revealed that Mn migration and cathode densification were occurring. The rate at which densification occurred was a function of time and temperature, as expected. The porosity and microstructure of the cathodes were examined on the SEM. A semi-quantitative examination of the Mn migration was accomplished on the SEM with an EDS/ZAF elemental analysis.

A/I/CE TRILAYER

Figure 3-47. Concentration Profile of Ca, Co, La, and Cr Across A/I/CE Trilayer

B-27001

Figure 3-48. XRD Pattern of Anode in A/I/CE Trilayer

B-27002

Figure 3-49. Sintering Shrinkage Profiles of Baseline and Toughened Anodes (A)

Figure 3-50. Sintering Shrinkage Profiles of Baseline and Toughened Cathode/Electrolyte Intermediates (CE)

Figure 3-51. Cathode Area Specific Interfacial Resistance for CE/E/CE Composite at 1200°C in Air vs Time

The Mn-concentration profile into the electrolyte from the cathode/electrolyte interface for the composites before and after the 1000°, 1100°, 1200°C tests is given in Figures 3-52, 3-53, and 3-54, respectively. Clearly, the penetration depth into the electrolyte increases with temperature. The fast rate at which the Mn concentration drops off with distance allows a definition of the penetration depth, since the distance into the electrolyte at which the Mn concentration drops is approximately 0.2 atomic percent. Table 3-13 gives the Mn depth of penetration as a function of time and temperature. There is a slight increase in depth in the 1000°C test over the length of the test, while in the 1100° and 1200°C tests, the change in depth occurs in the first 300 hr of test. Most of the changes occurred in the first part of the test, as shown graphically in Figure 3-55, which compares the Mn concentration profile at 173 and 1045 hr in the 1200°C test. It is significant that the electrolyte particles in the cathode (CE) layer are surely saturated with Mn (probably at about 2 atomic percent) after the firing of the composites.

The change in porosity during the tests is also included in Table 3-13. Generally, the porosity decreased over the length of the test, and the rate of decrease increases with the test temperature. Even with a porosity of only 6 percent, the cathode did not exhibit any bulk gas transport limitation, although from Table 3-13 it is clear that the performance of that electrode was not good (ASR = 0.569 ohm cm² at 1000°C).

Figure 3-52. Mn Concentration Profile in Electrolyte for CE/E/CE Composite at 1000°C After 1000 hr

Figure 3-53. Mn Concentration Profile in Electrolyte for CE/E/CE Composite at 1100°C After 1043 hr

Figure 3-54. Mn Concentration Profile in Electrolyte for CE/E/CE Composite at 1200°C After 1045 hr

TABLE 3-13					
COMPILATION OF RESULTS ON CE/E/CE COMPOSITES (SC 1193)					
Time, hr	Temperature, °C	Porosity, percent	Depth of Mn Penetration, μm	Average Interfacial Resistance in Ohm cm ²	
				Room Temperature	1000°C
0	1000	13.8	13	0.115	0.115
305	1000	13.2	13	0.122	0.122
665	1000	14.8	14	0.130	0.130
1000	1000	13.0	17	0.141	0.141
0	1100	13.8	13	0.080	0.115
266	1100	12.4	20	0.097	0.193
616	1100	11.8	15	0.107	
1043	1100	10.1	23	0.122	0.256
0	1200	13.8	13	0.063	0.115
173	1200	12.2	32	0.102	0.284
600	1200	9.6	30	0.122	
1045	1200	6.0	30	0.148	0.569

Figure 3-55. Mn Concentration Profiles in Electrolyte for CE/E/CE Composite at 1200°C After 173 hr and 1045 hr

Because the porosity decreases continuously with time and most of the Mn migration occurs in the first part of the test, the increase in the interfacial resistance with time can be attributed to the densification of the cathode. The rate of sintering of a ceramic layer has been examined theoretically for a single phase (References 3-1 and 3-2).^{*} Generally, the functionality in time varies according to the sintering mechanism and the stage of processing, but because it is basically a diffusional mechanism, the density change is approximately proportional to the square root of time. If it can be assumed that the change in interfacial resistance follows a similar function in time, then Equation 3-1 can be written:

$$(ASR) = (ASR)_0 + A(t+t_0)^{0.5} \quad (3-1)$$

In Equation 3-1, (ASR) is the area specific resistance of the cathode, t is time, and $(ASR)_0$, A , and t_0 are constants. Furthermore, since the constant A should be proportional to the solid-state diffusion coefficient, A should vary with temperature according to an Arrhenius expression given in Equation 3-2.

$$A = A_0 \exp (-E/RT) \quad (3-2)$$

Where A_0 is the pre-exponential factor, E is the activation energy for the process, R is the gas constant, and T is temperature.

^{*}References are presented in para 3.3.1.1.

The 1100° and 1200°C results from the CE/E/CE composites were used in obtaining the constants in Equation 3-1. The values of the constants are given in Table 3-14, and the fit of the experimental data are given in Figures 3-50 and 3-51, with the solid lines being the theoretical results. While Equation 3-1 fits the 1100° and 1200°C results relatively well, it is difficult to obtain the constants for the 1000°C data because the data are approximately linear. For the 1000°C results, the constant A was determined from the 1100° and 1200°C data using Equation 3-2 ($E = 1.2$ eV, $A_0 = 23.8$ ohm-cm²-hr^{-0.5}). The fit of the data is given in Figure 3-49, and the values of the other constants are given in Table 3-14. The value of the activation energy is the value that would be expected for a solid-state diffusional process.

TABLE 3-14				
COMPILATION OF CURVE FITTING PARAMETERS FOR EQUATION 3-1 BASED ON DATA FROM THE CE/E/CE COMPOSITES (SC 1193)				
Composite Designation	Temperature, °C	A, Ohm cm ² -hr ^{-0.5}	(ASR) ₀ , Ohm cm ²	t ₀ , hr
A	1200	0.0029	0.068	0
B	1200	0.0025	0.049	0
I	1100	0.0013	0.064	8
J	1100	0.0014	0.087	9
N	1000	0.00065*	0.120	14
M	1000	0.00065*	0.105	16
*Calculated from Equation 3-2 and the higher temperature data.				

The long-term effects of operation on the cathode can now be estimated with Equation 3-1. At 1000°C, if a 0.1 ohm-cm² change in the interfacial resistance is acceptable over the life of the fuel cell, the operating life would be over 23,000 hr. This change of 0.1 ohm-cm² corresponds to a reduction in cell potential of 50 mv at 0.5 amp/cm². Even if the 1000°C data are linearly extrapolated, the life of the fuel cell would be 4000 to 5000 hr. From these order-of-magnitude calculations, it can be assumed that the cathode studied would be acceptable for the long-term operation of the fuel cell. To reach this conclusion, the cathode must be operated for the life of the fuel cell. It is also assumed that degradation of the cathode by some catastrophic mechanism, such as delamination, would not occur. The mechanisms of interfacial reactions of two fuel cells (EE 068-06 and EE 068-03) were examined.

Posttest examination of the symmetric cathode composites concentrated on looking for the presence of La₂Zr₂O₇ in the CE layers of the CE/E/CE composites and examining the C/E/C and C/CE/E/CE/C.

To determine whether any $\text{La}_2\text{Zr}_2\text{O}_7$ is formed in the cathode during firing and subsequent testing, an X-ray diffraction analysis was performed on three cathode samples (from CE layers) and two original starting powder samples (doped ZrO_2 and LaMnO_3). The cathode samples were obtained from CE/E/CE composites (SC 1193) as fired, after 1000 hr at 1000°C , and after 1000 hr at 1200°C . As expected, the starting powders showed no trace of $\text{La}_2\text{Zr}_2\text{O}_7$. However, the as-fired CE sample has approximately 23 percent $\text{La}_2\text{Zr}_2\text{O}_7$ (atomic percent). No detectable increase in the $\text{La}_2\text{Zr}_2\text{O}_7$ was measured after 1000 hr at 1000°C (measured value 22 percent). The concentration of $\text{La}_2\text{Zr}_2\text{O}_7$ did increase to 33 percent after 1000 hr at 1200°C .

A second series of 1000-hr tests on C/E/C (SC 1198) and C/CE/E/CE/C (SC 1199) composites was completed. The electromechanical performance of the composites in air at 1000° , 1100° , and 1200°C was monitored as described above. The area specific resistance of the C/E/C and C/CE/E/CE/C composite cathode/electrolyte interfaces at 1000° , 1100° , and 1200°C are given in Figures 3-56 and 3-57, respectively. Generally, the results from the C/CE/E/CE/C composites are similar to those obtained on the CE/E/CE composites. In addition to the interfacial resistance being higher on the C/E/C composites, the 1200°C data exhibited a large increase in resistance starting at about 65 hr. When a C/E/C composite sample was removed from the 1200°C furnace at 300 hr, it was at least partially delaminated.

Posttest examination results of the C/E/C and C/CE/E/CE/C composite tests are given in Tables 3-15 and 3-16, respectively. Generally the results were similar to the earlier results obtained on the CE/E/CE composites. There are, however, a couple of notable differences. First, the decrease in porosity was not as great for the C/E/C and the C/CE/E/CE/C composites as those for the CE/E/CE. Also, the penetration of Mn into the electrolyte was not as great for the C/E/C composites compared with the other two sets.

Ac impedance was used to examine the initial interfacial and bulk resistance of fuel cell EE 068-06 at an established set of conditions (temperature, 1000°C ; fuel, $\text{H}_2/\text{H}_2\text{O}=97/3$; oxidant, air). The total area-specific resistance of the fuel cell was 0.866 ohm-cm^2 , of which 0.068 ohm-cm^2 was interfacial. The total resistance of the fuel cell is acceptable for testing, but it is not one of the top performing fuel cells ever tested.

An initial polarization sweep of the fuel cell (EE 068-06) under the established conditions described above and also with oxygen as the oxidant, is given in Figure 3-58. The characteristic reduction in slope with increase in current density of the oxygen polarization curve is apparent, although the slope of the polarization curve does not level off as much as has been observed in other cells tested. A series of experiments to examine possible mechanisms for this was conducted. Complicating these studies is the fact that the performance of the cell degrades with time. This can be seen in Figure 3-59, where a polarization curve was taken on the cell under the same conditions two days apart. While this degradation of performance is much more pronounced than the average, it does serve to illustrate an important point. At least some of the performance loss can be attributed to the degradation of the seal between the anode and cathode, which can be seen from the loss in open-circuit voltage. As a result of this,

Figure 3-56. C/E/C Composite Area Specific Interfacial Resistance vs Time in Air

Figure 3-57. C/CE/E/CE/C Composite Area Specific Interfacial Resistance vs Time in Air

TABLE 3-15			
COMPILATION OF POSTTEST RESULTS ON C/E/C COMPOSITES (SC 1198)			
Time, hr	Temperature, °C	Porosity, percent	Depth of Mn Penetration, microns
0	1000	22.2	0
433	1000	24.5	0
1053	1000	22.3	16
0	1100	22.2	0
262	1100	25.6	0
1051	1100	22.0	13
0	1200	22.2	0
329	1200	22.1	21
939	1200	13.6	29

TABLE 3-16			
COMPILATION OF POSTTEST RESULTS ON C/CE/E/CE/C COMPOSITES (SC 1198)			
Time, hr	Temperature, °C	Porosity, percent	Depth of Mn Penetration, microns
0	1000	17.9	24
433	1000	19.8	17
1053	1000	18.1	20
0	1100	17.9	24
262	1100	16.8	44
1051	1100	16.1	31
0	1200	17.9	24
329	1200	15.8	47
939	1200	15.2	52

only data obtained during a time when the cell performance did not degrade significantly are compared (i.e., data taken on different days were not compared).

A series of polarization curves was taken on the fuel cell (EE 068-06) in which the cathode atmosphere was varied and the temperature and fuel were kept constant.

Figure 3-58. Polarization Curves of Fuel Cell EE 068-06 at 1000°C and $H_2/H_2O = 97/3$ Fuel with the Indicated Oxidant

Figure 3-59. Polarization Curves of Fuel Cell EE 068-06 at 1000°C, Air as the Oxidant, and $H_2/H_2O = 97/3$ Fuel Taken on the Indicated Dates

Figure 3-60 compares the polarization curve of the fuel as a function of oxygen content in the cathode gas. Figure 3-61 compares the polarization curve of the fuel cell with air being the oxidant and also with a mixture of O_2 and He, where the O_2 content in both curves is the same. Referring to Figure 3-60, the high oxygen content curve exhibits the leveling off effect that was mentioned above. Figure 3-61 contains a direct comparison of the fuel cell with and without N_2 in the oxidant gas. Although this is just one test, since both curves in Figure 3-61 are basically the same, it is not likely that the production of NO_x significantly affects the cathode performance.

Ac impedance was used to examine the initial interfacial and bulk resistance of fuel cell EE 068-03 at an established set of conditions (temperature, $1000^\circ C$; fuel, $H_2/H_2O=97/3$; oxidant, air). The total area specific resistance of the fuel cell was 0.698 ohm-cm^2 , of which 0.427 ohm-cm^2 was interfacial. The total resistance of this fuel cell was lower than that of fuel cell EE 068-06, even though both were made from the same batch of material. Differences may be attributed to either the gas seal or possible cracks in the cell near the seal area.

A polarization sweep of the fuel cell (EE 068-03) under the established conditions described above, and also with oxygen and diluted air as the oxidant, is given in Figure 3-62. Although the fuel cell performed better than its sister cell tested earlier, the shapes of the curves were generally the same. Two polarization curves, given in Figure 3-63, were taken on the fuel cell in which the anode atmosphere was varied and the temperature and oxidant were kept constant. Except for the expected lower open-circuit potential and a slightly more linear polarization curve, the curves are very similar to each other.

Individual cell tests (see above and the Final Report for the METC 1 contract) conducted at Argonne and at ABB (formerly Combustion Engineering) indicated that the MSOFC performed much better on oxygen than on air as the oxidant gas (at $1000^\circ C$ with $H_2/H_2O=97/3$ as the fuel). This increase in performance is readily apparent due to the reduction in the slope of the fuel cell polarization (I-V) curve with increasing current density. In these tests at high current density, the slope of the polarization curve approaches the predicted bulk resistance of the electrolyte alone. The slope of the polarization curve in at least one test dropped below the predicted bulk resistance value, but with the inaccuracy of the cell area determination and noise in the data, the observation could not be established as reproducible. Generally, as the partial pressure of oxygen in the cathode gas is reduced, the decrease in the slope of the I-V curve with current becomes less, and the curve becomes more linear. At some point during the reduction of the partial pressure of oxygen, the opposite effect is observed and there is a sudden increase in the slope of the I-V curve with current that is observed at high current densities.

In developing a model to describe the observed effects, one must be consistent with other electrochemical studies conducted in this laboratory on fuel cells and symmetric composites such as ac impedance studies and current step experiments. Also, the model must be generally consistent with other established work in the field. As the first step in the modeling process, a reexamination of previous work inside and outside of this laboratory was performed. There are several aspects of the fuel cell that are

Figure 3-60. Polarization Curves of Fuel Cell EE 068-06 at 1000°C, and $H_2/H_2O = 97/3$ Fuel with Indicated Oxidant

Figure 3-61. Polarization Curves of Fuel Cell EE 068-06 at 1000°C, and $H_2/H_2O = 97/3$ Fuel with Indicated Oxidant

Figure 3-62. Polarization Curves of Fuel Cell EE 068-03 at 1000°C, and $H_2/H_2O = 97/3$ Fuel with Indicated Oxidant

Figure 3-63. Polarization Curves of Fuel Cell EE 068-03 at 1000°C, Oxygen as the Oxidant, and the Indicated H_2/H_2O Ratio

generally well established and should be included in the model. First, the electrolyte itself has been studied in depth for quite some time and has well-established properties (ionic and electronic conductivities) (References 3-3, 3-4). Both the anode and cathode are mixed-conductor (electronic and ionic) porous electrodes and should be modeled as such (Reference 3-5). Order-of-magnitude calculations on the rate of gas phase transport in the electrodes indicate that the electrochemical reactions are not generally gas phase limited, but gas phase transport will be included because in certain cases (e.g., low porosity in the cathode), it may become important. There are many transport and kinetic phenomena associated with the three-phase (electrode material/electrolyte material/gas) electrochemically active area in each electrode; the importance of these are not well established and are subject to some debate (References 3-6 and 3-7)).

Of the many postulated interfacial phenomena, three that will be included are surface adsorption and diffusion (References 3-8 and 3-9) of reactants and products, and electrochemical kinetics (References 3-6, 3-7). These are generally accepted as important, and evidence from ac impedance studies performed at Argonne support this importance. These phenomena alone will not completely explain the previously discussed I-V curve for MSOFC's. To account for the observed decrease in slope with current density, one must have a second reaction mechanism for each electrode, i.e., one reaction mechanism that is governing near equilibrium and another applicable at high currents. Possible explanations for the behavior can be found in the work of Kliez, et. al. (References 3-10 and 3-11).

For the cathode, Kliez et. al. (Reference 3-10) have postulated that at low currents near equilibrium, the doped LaMnO_3 acts as a metal electrode material, but that at high currents, the Mn is partially reduced, forming oxygen vacancies. These oxygen vacancies allow the electrochemical reaction to occur on the electrode material, thus expanding the electrochemically active area. This dual-path reaction mechanism for the cathode would help explain the observed behavior.

In earlier work on anodes in reducing (hydrogen) environments, Kliez et al. (also at Argonne) observed that adding H_2O to the gas reduced the interfacial resistance to effectively zero (Reference 3-11). Kliez postulated that the H_2O adsorbed on the surface of the electrolyte created an electronically conducting layer that enhanced the electrochemical reaction by creating a second path for electrons to get to the reaction sites. Another, more plausible, explanation would be that the water adsorbed on the surface of the electrolyte allows fast protonic conduction to occur on the surface. This explanation would be consistent with the fact that adding approximately 3 percent H_2O to the cathode gas does not reduce the interfacial resistance. If water is slow to desorb from the electrolyte surface, the H_2O surface concentration on the electrolyte will increase with current density, thus reducing the anode interfacial resistance. A mathematical model incorporating the interfacial and bulk effects described above would account for the observed behavior in MSOFC's.

3.3.1.1 References

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3.3.2 Theory of Interfacial and Bulk Phenomena

Quantitative transport and interfacial reaction equations for an electrochemical model of a three-layer (A/E/CE) composite fuel cell were developed. Each of the electrode layers is made up of three phases; nickel (anode) or Sr-doped LaMnO_3 (cathode), $\text{ZrO}_2\text{-Y}_2\text{O}_3$ electrolyte, and gas. The gas phase for the anode is a mixture of H_2 and H_2O , and for the cathode is a mixture of O_2 and N_2 . One-dimensional (in the y-direction) volume-averaged transport equations are used to describe these phenomena. The edge of the anode is considered to be y equal to 0, with the anode-electrolyte interface at y_1 , the cathode-electrolyte interface at y_2 , and the total thickness of the composite being L. The electrolyte layer is considered to be dense.

A steady-state mass balance on each specie in each phase can be written and is given in Equation (1). A listing of the notations used in this and subsequent equations is shown in para. 3.3.2.1:

$$0 = -\nabla N_i + a_k j_i + \epsilon_k R_i \quad (1)$$

For the gas phases, the relationship between the flux of specie i and its concentration gradient is given by the Stefan-Maxwell equation (Equation (2) for an ideal gas):

$$\nabla X_i = \sum_j \frac{\tau_k}{c D_{ij} \epsilon_k} (X_i N_j - X_j N_i) \quad (2)$$

Equation (2) modifies the Stefan-Maxwell equation by multiplying the diffusion coefficient by the volume fraction over the tortuosity of the gas phase to account for the multiple phases in the electrodes. The assumption of an ideal gas also gives the relationships in Equations (3) and (4):

$$P = c R T \quad (3)$$

$$p_i = X_i P \quad (4)$$

Specifically for the two components in the cathode gas phase, one can write Equations (5) and (6).

$$X_{O_2} + X_{N_2} = 1 \quad (5)$$

$$\nabla X_{O_2} = \frac{\tau_c}{c D_{O_2-N_2} \epsilon_c} (X_{O_2} N_{N_2} - X_{N_2} N_{O_2}) \quad (6)$$

Since nitrogen does not react in the electrode at steady state, the flux of nitrogen is 0 (Equation (7)):

$$N_{N_2} = 0 \quad (7)$$

The mass balance for oxygen in the cathode gas phase is given by Equation (8), which was obtained by combining Equations (1) through (7):

$$0 = a_c j_{O_2} + \frac{P D_{O_2-N_2} \epsilon_c}{RT \tau_c} \frac{\partial}{\partial y} \left[\frac{\frac{\partial p_{O_2}}{\partial y}}{P - p_{O_2}} \right] \quad (8)$$

Similarly, for the two components in the anode gas phase, Equations (9) and (10) can be written:

$$\nabla X_{H_2} = \frac{\tau_a}{c D_{H_2-H_2O} \epsilon_a} (X_{H_2} N_{H_2O} - X_{H_2O} N_{H_2}) \quad (9)$$

$$X_{H_2} + X_{H_2O} = 1 \quad (10)$$

Since in the anode the hydrogen reacts to form water in equal molar quantities, one can write Equation (11) at steady state:

$$N_{H_2} = - N_{H_2O} \quad (11)$$

As with the cathode gas phase, the above equations can be combined to obtain the mass balance for the hydrogen in the anode gas phase (Equation (12)):

$$0 = a_a j_{H_2} + \frac{D_{H_2-H_2O} \epsilon_a}{RT \tau_a} \frac{\partial^2 p_{H_2}}{\partial y^2} \quad (12)$$

For the solid phases ($LaMnO_3$, Ni, and ZrO_2), it is assumed that dilute solution equations (Equation (13)) are applicable for the flux of vacancies, electrons, and holes in the zirconia, as well as for electrons in the nickel and holes in the $LaMnO_3$:

$$N_i = - z_i F c_i \frac{u_i \epsilon_k}{\tau_k} \nabla \phi_k - \frac{D_i \epsilon_k}{\tau_k} \nabla c_i \quad (13)$$

Combining Equations (1) and (13) results in Equation (14), which is applicable for each of the mobile species in the solid phases. Further, because these mobile species are charged, the requirement of electroneutrality, given in Equation (15), is needed to describe the transport of the mobile species:

$$0 = a_k j_i + z_i F \frac{u_i \epsilon_k}{\tau_k} \nabla (c_i \nabla \phi_k) + \frac{D_i \epsilon_k}{\tau_k} \nabla^2 c_i + \epsilon_k R_i \quad (14)$$

$$0 = \sum_i z_i c_i \quad (15)$$

For the Sr-doped $LaMnO_3$ and the nickel phases, it is assumed that the concentration of the mobile species does not vary. It is further assumed that the mobile species in the nickel phase are electrons and that the mobile species in the $LaMnO_3$ phase are holes. This is a good assumption for the nickel, since it is a metal. It is also a good

assumption for the Sr-doped LaMnO_3 phase, which is a p-type semiconductor. Sr-doped LaMnO_3 is also known to be an oxygen vacancy conductor, but work by Kleitz et al. suggests that the vacancy conduction is important only near the three-phase ($\text{LaMnO}_3\text{-ZrO}_2\text{-H}_2/\text{H}_2\text{O}$) interface and that it can be accounted for by the interfacial reaction equations. With the above assumptions, Equation (14) can be reduced to Equation (16) for the LaMnO_3 phase and to Equation (17) for the nickel phase, where the conductivity is defined in Equations (18) and (19):

$$0 = a_c F z_h \cdot j_{lh} + \frac{\kappa_1 \epsilon_1}{\tau_1} \frac{\partial^2 \phi_c}{\partial y^2} \quad (16)$$

$$0 = a_n F z_e \cdot j_{ne} + \frac{\kappa_n \epsilon_n}{\tau_n} \frac{\partial^2 \phi_n}{\partial y^2} \quad (17)$$

$$\kappa_i = F^2 z_i^2 \frac{u_i \epsilon_k}{\tau_k} c_i \quad (18)$$

$$\kappa_k = \sum_i \kappa_i \quad (19)$$

For the zirconia electrolyte phase, the concentration of oxygen vacancies is determined by the level of yttria doping and is, to a very good approximation, constant. With this assumption, Equation (14) for the vacancy concentration reduces to Equation (20):

$$0 = a_k j_{V_0} + F z_{V_0} \cdot \frac{u_{V_0} \epsilon_k}{\tau_k} c_{V_0} \frac{\partial^2 \phi}{\partial y^2} \quad (20)$$

Conversely, the electron and hole concentration in the zirconia phase is a strong function of oxygen partial pressure. As with many semi-conductors, the electrons and holes can react as shown in Equation (21):

From the above reaction, it is clear that the bulk production rates of electrons and holes are equal, as given in Equation (22):

$$R_{e^-} = R_{h^+} \quad (22)$$

Substituting Equation (14) for the electron and hole concentration in Equation (22) and rearranging its elements yields Equation (23):

$$0 = a_k(j_{e-} - j_{h+}) + \left[z_{e-} F \frac{u_{e-} \epsilon_k}{\tau_k} \frac{\partial}{\partial y} \left[c_{e-} \frac{\partial \Phi}{\partial y} \right] + \frac{D_{e-} \epsilon_k}{\tau_k} \frac{\partial^2 c_{e-}}{\partial y^2} \right] - \left[z_{h+} F \frac{u_{h+} \epsilon_k}{\tau_k} \frac{\partial}{\partial y} \left[c_{h+} \frac{\partial \Phi}{\partial y} \right] + \frac{D_{h+} \epsilon_k}{\tau_k} \frac{\partial^2 c_{h+}}{\partial y^2} \right] \quad [23] \quad (23)$$

Further, it is generally assumed that the electrons and holes are in equilibrium, producing Equation (24):

$$c_{e-} c_{h+} = n_i^2 \quad (24)$$

A complete set of transport equations for the fuel cell is described above. Expressions for the interfacial reaction terms (j_i) must now be developed. To develop these expressions, one must have a mechanism or mechanisms for the electrochemical reactions. As a first step in this process, a single reaction mechanism for each of the anode and cathode reactions is assumed. the dual reaction mechanism described in the last quarterly report will be implemented at a later date.

The electrochemical reaction at the three-phase interfacial area (nickel-zirconia- H_2/H_2O) in the anode is considered to occur through the following series of steps at discrete points; in reality, a distribution of effect exists, but the added mathematical complexity is not justified by the increase in accuracy:

- (a) H_2 is adsorbed onto the surface of the zirconia electrolyte.
- (b) H_2 diffuses along the surface to the reaction area.

(c) In the reaction area, the reaction in Equation (25) occurs:

- (d) H_2O diffuses along the electrolyte surface from the reaction zone.
- (e) H_2O is desorbed into the gas phase from the zirconia electrolyte surface.
- (f) Electrons diffuse from the reaction zone into the bulk electrolyte.
- (g) Electrons diffuse from the bulk electrolyte to the nickel-electrolyte interface.
- (h) Electrons pass from the zirconia phase to the nickel phase according to the reaction in Equation (26):

The reactions in Equations (25) and (26) are a source and/or sink for electrons in the zirconia electrolyte phase of the anode (Equation (27)):

$$j_{\text{e}^-} = j_{\text{ae}^-} + j_{\text{ge}^-} \quad (27)$$

The electron reaction in Equation (26) is clearly an electrochemical reaction and is treated as such with its rate given in Equation (28):

$$\begin{aligned} j_{\text{ae}^-} = - \frac{(\bar{i}_0)_n}{n_n F} \left[\frac{c_{\text{ne}^-}}{(c_{\text{e}^-})_{\text{ref}}} \right]^{\beta_n} \left[\exp \left[\frac{(1 - \beta_n) n_n F}{RT} (\Phi_a - \Phi) \right] - \right. \\ \left. \exp \left[- \frac{\beta_n n_n F}{RT} (\Phi_a - \Phi) \right] \right] \quad [28] \end{aligned} \quad (28)$$

Steps (b), (d), (f), and (g) above can be characterized mathematically by a concentration difference and a mass-transfer coefficient given in Equations (29) through (32):

$$j_{\text{ge}^-} = 2 K_{\text{sH}_2} (\theta_{\text{aH}_2} - \theta_{\text{rH}_2}) \quad (29)$$

$$j_{ge-} = 2 K_{sH_2O} (\theta_{rH_2O} - \theta_{aH_2O}) \quad (30)$$

$$j_{ge-} = K_{e-} (c_{ae-} - c_{e-}) \quad (31)$$

$$j_{ae-} = K_{e-} (c_{ne-} - c_{e-}) \quad (32)$$

The reaction in Equation (25) is assumed to be at equilibrium with the concentration of oxygen vacancies and oxygen ions considered constant. The equilibrium expression for the reaction is given in Equation (33):

$$K_{ae} = \frac{\theta_{rH_2O} (c_{ae-})^2}{\theta_{rH_2}} \quad (33)$$

The surface concentration of the gases at the point of adsorption/desorption is given in Equations (34) and (35):

$$\theta_{aH_2} = \frac{K_{H_2} P_{H_2}}{1 + K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}} \quad (34)$$

$$\theta_{aH_2O} = \frac{K_{H_2O} P_{H_2O}}{1 + K_{H_2} P_{H_2} + K_{H_2O} P_{H_2O}} \quad (35)$$

The production of H₂ into the gas phase and electrons into the nickel phase can be related to that of the electrolyte phase by the reaction equations and is given in Equations (36) and (37):

$$j_{H_2} = - \frac{1}{2} j_{ge-} \quad (36)$$

$$j_{ne-} = - j_{ae-} \quad (37)$$

A cathode reaction mechanism similar to that of the anode is as follows:

- (a) O₂ disassociates and adsorbs onto the zirconia electrolyte surface.
- (b) Disassociated O₂ diffuses along the surface to the reaction zone.

(c) The reaction in Equation (38) occurs in the reaction area:

(d) Holes diffuse from the reaction zone into the bulk electrolyte.

(e) Holes diffuse from the bulk electrolyte to the LaMnO₃-electrolyte interface.

(f) Holes pass from the zirconia phase to the LaMnO₃ phase according to the reaction in Equation (39):

Equations (40) through (48) mathematically describe the above steps:

$$j_{h^{\cdot}} = j_{ch^{\cdot}} + j_{gh^{\cdot}} \quad (40)$$

$$\begin{aligned} j_{ch^{\cdot}} = \frac{(i_o)_1}{n_1 F} &\left[\frac{c_{1h^{\cdot}}}{(c_{h^{\cdot}})_{\text{ref}}} \right]^{(1-\beta_1)} \left[\exp \left[\frac{(1-\beta_1)n_1 F}{RT} (\Phi_c - \Phi) \right] \right. \\ &\left. - \exp \left[- \frac{\beta_1 n_1 F}{RT} (\Phi_c - \Phi) \right] \right] \quad [41] \end{aligned} \quad (41)$$

$$j_{ch^{\cdot}} = K_h \cdot (c_{1h^{\cdot}} - c_{h^{\cdot}}) \quad (42)$$

$$K_{ce} = \frac{(1 - \theta_{r0}) (c_{ch^{\cdot}})^2}{\theta_{r0}} \quad (43)$$

$$j_{gh^{\cdot}} = K_h \cdot (c_{ch^{\cdot}} - c_{h^{\cdot}}) \quad (44)$$

$$j_{gh^{\cdot}} = 2 K_{s0} (\theta_{a0} - \theta_{r0}) \quad (45)$$

$$\theta_{a0} = \frac{K_{O_2} (p_{O_2})^{1/2}}{1 + K_{O_2} (p_{O_2})^{1/2}} \quad (46)$$

$$j_{O_2} = -\frac{1}{2} j_{gh} \quad (47)$$

$$j_{lh} = -j_{ch} \quad (48)$$

The above equations can be used to determine the cell voltage by setting the current through the cell (Equation (49)) and the gas partial pressures outside of the anode and cathode.

$$i = \sum_i z_i F N_i \quad (49)$$

The complexity of the equations requires the system to be solved numerically. An existing, off-the-shelf program has been used to accomplish this. Besides making the solution of the problem easier, the program allows the faster incorporation of changes and improvements in the model.

After solving a series of small problems, the program is now running using a representative set of parameters. The results of a series of calculations are given in Figure 3-64. The calculations show the change in the current-voltage relationship of the fuel cell as various effects are added to the model. The parameters for the model were either obtained from established literature results or were extracted from alternating current impedance data on symmetric composites.

Figure 3-64. Electrochemical Model Results with the Indicated Effects Incorporated in the Calculations

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3.3.2.1 Equation Elements

- a_a : Active area per unit volume in the anode, cm^2/cm^3
- a_c : Active area per unit volume in the cathode, cm^2/cm^3
- a_k : Active area per unit volume in specific phase k , cm^2/cm^3
- c : Total concentration in gas phase, moles/cm^3
- c_i : Bulk concentration of species i in specific phase k ,
 moles/cm^3
- c_{e-} : Concentration of electrons in the bulk electrolyte,
 moles/cm^3
- c_{ne-} : Concentration of electrons in the electrolyte phase of
the anode at the nickel-electrolyte reaction zone,
 moles/cm^3
- c_{ae-} : Concentration of electrons in the electrolyte phase of
the anode at the gas-electrolyte reaction zone, moles/cm^3
- c_{lh} : Concentration of holes in the electrolyte phase of
the cathode at the LaMnO_3 -electrolyte reaction zone,
 moles/cm^3
- c_{ch} : Concentration of holes in the electrolyte phase of the
cathode at the gas-electrolyte reaction zone, moles/cm^3
- c_h : Concentration of holes in the electrolyte phase, moles/cm^3
- c_{V_0} : Concentration of oxygen vacancies in the electrolyte
phase, moles/cm^3
- $(c_{e-})_{\text{ref}}$: Reference concentration of electrons in the
electrolyte phase, mole/cm^3
- $(c_h)_{\text{ref}}$: Reference concentration of holes in the
electrolyte phase, mole/cm^3
- D_i : Diffusion coefficient of species i in specific solid
phase k , cm^2/sec
- D_{ij} : Binary diffusion coefficient of species i and j in
a gas phase, cm^2/sec
- D_{e-} : Diffusion coefficient of electrons in the electrolyte
phase, cm^2/sec
- D_h : Diffusion coefficient of holes in the electrolyte
phase, cm^2/sec

D_{V_0} : Diffusion coefficient of vacancies in the electrolyte phase, cm^2/sec
 $D_{\text{H}_2-\text{H}_2\text{O}}$: Binary diffusion coefficient for H_2 and H_2O in the anode gas phase, cm^2/sec
 $D_{\text{O}_2-\text{N}_2}$: Binary diffusion coefficient of oxygen and nitrogen in the cathode gas phase, cm^2/sec
 e^- : Designation for an electron
 F : Faraday's constant, 96487 C/equiv
 h^+ : Designation for hole
 H_2 : Designation for hydrogen
 H_2O : Designation for water
 i : Current density in a phase, A/cm^2
 I : Set cell current density, A/cm^2
 $(i_o)_n$: Exchange current density for electron transfer reaction from the nickel phase to the electrolyte phase in the anode at reference concentrations, A/cm^2
 $(i_o)_1$: Exchange current density for the hole transfer reaction from the LaMnO_3 phase to the electrolyte phase in the cathode at reference concentrations, A/cm^2
 j_i : Net production rate of species i per active area in phase k , $\text{mole}/\text{sec}\text{-cm}^2$
 j_{O_2} : Net oxygen production rate per active area in the cathode gas phase, $\text{mole}/\text{sec}\text{-cm}^2$
 j_{H_2} : Net hydrogen production rate per active area in the anode gas phase, $\text{mole}/\text{sec}\text{-cm}^2$
 j_{e^-} : Net electron production rate per active area in the electrolyte phase, $\text{mole}/\text{sec}\text{-cm}^2$
 j_{h^+} : Net hole production rate per active area in the electrolyte phase, $\text{mole}/\text{sec}\text{-cm}^2$
 j_{ne^-} : Net electron production rate per active area in the nickel phase, $\text{mole}/\text{sec}\text{-cm}^2$

j_{lh} : Net hole production rate per active area in the LaMnO_3 phase, mole/sec-cm²
 j_{ae} : Electron production rate per active area in the electrolyte phase from the nickel phase, mole/sec-cm²
 j_h : Hole production rate per active area in the electrolyte phase from the LaMnO_3 phase, mole/sec-cm²
 j_{ge} : Electron production rate per active area in the electrolyte phase from the anode gas phase, mole/sec-cm²
 j_{gh} : Hole production rate per active area in the electrolyte phase from the cathode gas phase, mole/sec-cm²
 j_{V_0} : Net vacancie production rate per active in the electrolyte phase, mole/sec-cm²
 K_{H_2} : Hydrogen adsorption coefficient, atm⁻¹
 K_{H_2O} : Water adsorption coefficient, atm⁻¹
 K_{O_2} : Oxygen adsorption coefficient, atm^{-1/2}
 K_{sH_2} : Surface mass transfer coefficient for H_2 on the electrolyte surface in the anode, mole/sec-cm²
 K_{sH_2O} : Surface mass transfer coefficient for H_2O on the electrolyte surface in the anode, mole/sec-cm²
 K_{sO_2} : Surface mass transfer coefficient for O_2 on the electrolyte surface in the cathode, mole/sec-cm²
 K_{e-} : Mass transfer coefficient for electrons in the electrolyte phase of the anode between the interface and the bulk, cm/sec
 K_{h-} : Mass transfer coefficient for holes in the electrolyte phase of the cathode between the interface and the bulk, cm/sec
 L : Total composite thickness, cm
 N_2 : Designation for nitrogen
 N_i : Molar flux of species i, mole/sec-cm²
 N_j : Molar flux of species j, mole/sec-cm²
 N_O : Molar flux of oxygen, mole/sec-cm²

$N_{N_2}^2$: Molar flux of nitrogen, mole/sec-cm²
 $N_{H_2}^2$: Molar flux of hydrogen, mole/sec-cm²
 $N_{H_2O}^2$: Molar flux of water, mole/sec-cm²
 N_i^2 : Equilibrium constant for electrons and holes in the electrolyte, mole²/cm⁶
 n_n : Number of electrons transferred from the nickel phase to the electrolyte phase in the anode
 n_1 : Number of holes transferred from the LaMnO₃ phase to the electrolyte phase in the cathode
 O_2 : Designation for oxygen
 O_0^x : Designation for an oxygen ion at an oxygen ion lattice site
 p_i : Partial pressure of species i in a gas phase, atm
 P : Total pressure in the gas phases, atm
 P_{H_2} : Partial pressure of H₂ in anode gas phase, atm
 P_{H_2O} : Partial pressure of H₂O in anode gas phase, atm
 P_{O_2} : Partial pressure of O₂ in cathode gas phase, atm
 P_{N_2} : Partial pressure of N₂ in cathode gas phase, atm
 R : Universal gas Constant, 8.3143 J/mole-K
 R_i : Net bulk rate of production of species i, mole/sec-cm³
 R_{e-} : Net bulk rate of production of electrons in the electrolyte phase, mole/sec-cm³
 R_h : Net bulk rate of production of holes in the electrolyte phase, mole/sec-cm³
 T : Temperature, K
 u_i : Mobility of species i, cm²-mole/J-sec
 u_{e-} : Mobility of electrons in the electrolyte, cm²-mole/J-sec
 u_h : Mobility of electrons in the electrolyte, cm²-mole/J-sec
 u_{V_0} : Mobility of electrons in the electrolyte, cm²-mole/J-sec
 V_0 : Designation for a vacancy at an oxygen ion lattice site
 X_i : Mole fraction of specie i in a gas phase
 X_j : Mole fraction of specie j in a gas phase
 X_H : Mole fraction of H₂ in the anode gas phase

$x_{H_2O}^2$: Mole fraction of H_2O in the anode gas phase
 x_{N_2} : Mole fraction of N_2 in the cathode gas phase
 x_{O_2} : Mole fraction of O_2 in the cathode gas phase
 y : Normal distance, cm
 y_1 : Position of anode-electrolyte interface, cm
 y_2 : Position of cathode-electrolyte interface, cm
 z_i : Charge number of specie i
 z_{e-} : Charge number of electrons
 z_h : Charge number of holes
 z_{V_0} : Charge number of vacancies
 β_n : Symmetry factor for electron transfer reaction from the nickel phase to the electrolyte phase in the anode
 β_1 : Symmetry factor for electron transfer reaction from the $LaMnO_3$ phase to the electrolyte phase in the cathode
 Φ : Potential in the electrolyte phase, V
 Φ_a : Potential in the nickel phase of the anode, V
 Φ_c : Potential in the $LaMnO_3$ phase of the cathode, V
 Φ_k : Potential in the phase k , V
 κ_k : Conductivity of phase k , $1/\Omega\text{-cm}$
 κ_i : Conductivity of specie i in phase k , $1/\Omega\text{-cm}$
 κ_1 : Conductivity of $LaMnO_3$ phase, $1/\Omega\text{-cm}$
 κ_n : Conductivity of nickel phase, $1/\Omega\text{-cm}$
 τ_k : Tortuosity of phase k
 τ_n : Tortuosity of nickel phase in anode
 τ_1 : Tortuosity of $LaMnO_3$ phase in cathode
 τ_{ae} : Tortuosity of electrolyte in anode
 τ_{ce} : Tortuosity of electrolyte phase in cathode
 τ_a : Tortuosity of gas phase in anode
 τ_c : Tortuosity of gas phase in cathode
 ϵ_n : Volume fraction of nickel phase in anode
 ϵ_1 : Volume fraction of $LaMnO_3$ phase in cathode
 ϵ : Volume fraction of electrolyte phase in anode

ϵ_{ce} : Volume fraction of electrolyte phase in cathode
 ϵ_a : Volume fraction of gas phase in anode
 ϵ_c : Volume fraction of gas phase in cathode
 ϵ_k : Volume fraction of phase k
 θ_{aH_2} : Fractional surface coverage of H_2 on the electrolyte at an adsorption site in the anode
 θ_{aH_2O} : Fractional surface coverage of H_2O on the electrolyte at an adsorption site in the anode
 θ_{rH_2} : Fractional surface coverage of H_2 on the electrolyte at a reaction site in the anode
 θ_{rH_2O} : Fractional surface coverage of H_2O on the electrolyte at a reaction site in the anode
 θ_{aO_2} : Fractional surface coverage of O_2 on the electrolyte at an adsorption site in the cathode
 θ_{aN_2} : Fractional surface coverage of N_2 on the electrolyte at an adsorption site in the cathode
 θ_{rO_2} : Fractional surface coverage of O_2 on the electrolyte at a reaction site in the cathode
 θ_{rN_2} : Fractional surface coverage of N_2 on the electrolyte at a reaction site in the cathode

3.4 PERFORMANCE OF THE ANODE AND INTERCONNECT IN COAL GAS

The objective of this task was to evaluate the performance of the anode and interconnect materials during operation of the MSOFC on coal gas. The primary goal is to determine the effect of sulfur on the electrochemical performance of the anode and interconnect in simulated coal gas.

Platinum paste/screen current collectors were applied to a series of symmetric A/E/A (SC 1192) composites. Electrical contacts to one of the composites were made, and the composite was placed in a controlled-atmosphere tube and brought up to 1000°C in air. Once at temperature, the atmosphere of the composite was changed to H₂/H₂O (approximately 97/3). The anode/electrolyte interfacial resistance was monitored using ac impedance. The results are given in Figure 3-65. The interfacial resistance varied some in the first 40 hr, which is generally attributed to sintering of the Ni in the anode. After 50 hr the interfacial resistance remained relatively constant.

As an initial test for the sulfur sensitivity of the anode, H₂/H₂O atmosphere of the A/E/A composite was maintained, and 0.97 ppm H₂S was added. In the first few hours after the sulfur was introduced, there was a significant increase in the interfacial resistance. The interfacial resistance approximately doubled after 150 hr, when the H₂S concentration was increased to 1.8 ppm. After the change, there was another sudden increase in the interfacial resistance. The effects of H₂S concentrations up to 37.2 ppm on the anode/electrolyte interfacial resistance are shown in Figure 3-66, which shows that the interfacial resistance never reached a steady-state, even after more than 1300 hr of sulfur exposure. The extremely long time constant in the sulfur results indicate that something is probably changing the microstructure of the composite. One possibility might be that sulfur is being incorporated into the zirconia; an indication of this is the large increase in the bulk resistance of the composite shown in Figure 3-67.

The test was halted because the resistance measurements at the higher concentrations became erratic, as shown in the bulk resistance of the composite of Figure 3-67. Examination of the composite showed that the current collectors were still connected. Initial posttest studies indicated that the anodes on the composite were not the same. Optical micrographs show the difference in Ni concentration to be quite evident. The posttest examinations of the composite also indicated that the platinum penetrated relatively deeply into the electrode in places. This is the first time such a deep penetration of the platinum paste has been observed.

The sulfur effects of an A/E/A composite using an established ac impedance technique were examined in both H₂/H₂O and coal gas environments.

The change in the anode/electrolyte interfacial resistance for A/E/A composite EE 012-21, with time, during a series of studies on hydrogen and coal gas, is given in Figure 3-68. A series of diagnostic tests was conducted during the break in the data from 50 to 150 hr.

By comparing Figure 3-68 with the results on composite (SC 1192), the sulfur sensitivity is much less in the present composite. As expected, the sulfur sensitivity on

Figure 3-65. A/E/A Composite (SC 1192)

Figure 3-66. Anode Area Specific Interfacial Resistance for A/E/A (SC 1192) at 1000°C in H₂/H₂O = 97/3 vs Time

Figure 3-67. Area Specific Bulk Resistance for A/E/A (SC 1192) at 1000°C in $H_2/H_2O = 97/3$ vs Time

Figure 3-68. Area-Specific Interfacial Resistance of A/E/A Composite (EE 012-21) at 1000°C

coal gas does not seem to be significantly different from that of H_2/H_2O . Also, the initial interfacial resistance is higher than that for composite SC 1192, although it does decrease to a similar value.

The work on examining the sulfur effects of an A/E/A composite (EE 012-21) indicated an improved sulfur tolerance with the recent change in anode composition. A comparison between the performance of the new and old anode compositions in an H_2/H_2O atmosphere was conducted. As shown in Figure 3-69, the new anode composition (EE 068-09) and the old anode composition (SC 1192) performed similarly over the range of studies.

Figure 3-69. Interfacial Resistance of Anode in A/E/A Composites at 1000°C and H_2/H_2O Atmosphere with New (EE 068-09) and Old (SC 1192) Anode Composites

The sulfur sensitivity of another A/E/A composite (EE 068-11) was examined. The interfacial and bulk resistances as a function of time after being exposed to 1.14 ppm H_2S is given in Figures 3-70 and 3-71, respectively. While no sudden jump in resistance occurs with the addition of sulfur, there is a very clear increase over the time studied. Thus, sulfur does affect the long-term performance of the MSOFC.

3.5 STUDY OF MECHANICAL PROPERTIES

In this task the mechanical properties of partially and fully sintered MSOFC components were measured and compiled to form a data base for the computation of stress and strain conditions in MSOFC cells and stacks during sintering and operation.

Figure 3-70. Area-Specific Interfacial Resistance of A/E/A Composite (EE 068-11) at 1000°C

Figure 3-71. Area-Specific Bulk Resistance of A/E/A Composite (EE 068-11) at 1000°C

3.5.1 The Dependence of Anode, Electrolyte, and Cathode Mechanical Properties on Temperature

The density, strength, and elastic modulus of cathode, anode, and electrolyte specimens were measured at ANL. For these studies approximately 15 specimens of each component were fired at a specified temperature, progressing from 900° to 1350°C. The specimens were formed into discs approximately 1 in. in diameter and were approximately 10- to 14-mil thick. The results of the evaluations are shown in Tables 3-17, 3-18, and 3-19.

TABLE 3-17			
MEASURED PROPERTIES OF INTERMEDIATE (CATHODE) SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.35 ± 0.06	8.5 ± 0.38	9.61 ± 1.85
1000°C/0.0 hr	3.39 ± 0.05	12.8 ± 0.83	14.16 ± 3.63
1100°C/0.0 hr	3.42 ± 0.05	18.6 ± 0.73	25.50 ± 3.24
1200°C/0.0 hr	3.68 ± 0.14	29.3 ± 1.20	38.40 ± 7.00
1300°C/0.0 hr	4.45 ± 0.12	83.1 ± 7.20	49.30 ± 11.60
1350°C/0.0 hr	4.85 ± 0.14	105.1 ± 8.00	66.30 ± 7.70
1350°C/0.0 hr	5.01 ± 0.20	122.7 ± 10.20	63.30 ± 7.90

TABLE 3-18			
MEASURED PROPERTIES OF ANODE SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.24 ± 0.01	14.9 ± 1.81	7.51 ± 0.92
1000°C/0.0 hr	3.37 ± 0.17	16.7 ± 0.70	9.35 ± 1.80
1100°C/0.0 hr	3.43 ± 0.14	18.6 ± 0.73	20.65 ± 3.10
1200°C/0.0 hr	3.76 ± 0.01	30.9 ± 2.12	35.60 ± 5.89
1300°C/0.0 hr	4.68 ± 0.38	59.7 ± 9.94	64.74 ± 12.10
1350°C/0.0 hr	5.52 ± 0.23	134.0 ± 9.30	76.01 ± 15.80
1350°C/0.5 hr	5.68 ± 0.33	138.4 ± 19.80	101.30 ± 14.51

TABLE 3-19			
MEASURED PROPERTIES OF ELECTROLYTE SPECIMENS			
Heat Treatment, temp/time	Density, g/cc	Elastic Modulus, GPa	Biaxial Strength, MPa
900°C/0.0 hr	3.13 ± 0.04	16.35 ± 0.91	8.58 ± 1.22
1000°C/0.0 hr	3.13 ± 0.09	25.44 ± 2.08	15.41 ± 3.92
1100°C/0.0 hr	3.14 ± 0.38	53.11 ± 4.60	29.48 ± 10.13
1200°C/0.0 hr	3.55 ± 0.12	52.46 ± 4.13	63.80 ± 20.20
1300°C/0.0 hr	4.81 ± 0.12	149.13 ± 13.50	105.40 ± 33.31
1350°C/0.0 hr	5.03 ± 0.14	185.31 ± 8.30	126.70 ± 33.24
1350°C/0.5 hr	5.51 ± 0.40	212.35 ± 6.20	158.30 ± 40.12

3.5.2 Mechanical Properties of Calcium-, Cobalt-Doped Lanthanum Chromite Interconnect

The density, strength, and elastic modulus of the Ca-, Co-doped Lanthanum Chromite interconnect material were measured. Fifteen test discs 3 cm in diameter were cut from green tapes and sintered at 1400°C for 1 hr. The density has been measured as 6.15 ± 0.13 gm per centimeter cubed, the biaxial strength is 82 ± 20 MPa, and the elastic modulus is 273 ± 18 MPa. Weibull plots for failure probability (F) distribution of strength data for these specimens have been constructed, as shown in Figure 3-72. The Weibull modulus, m , was calculated from the slope of the lines on the plot to be 4.8. The small value of m suggests a large scatter in strength data.

3.5.3 Parametric Analysis of the Dependence of Electrolyte Mechanical Properties on Particle Size and Surface Area, Solids Loading, and Firing Temperature

ASE evaluated the density and mechanical properties of eight sets of electrolyte specimens with two different particle sizes (coarse and fine) and solids loading (45 and 55 vol%) fired at different sintering temperatures (1100° and 1400°C). Table 3-20 presents the identification and processing variables for the electrolyte specimens. The coarse specimens had a surface area of 6.4 meters-squared per gram. The fine specimens had a surface area of 16.6 meters-squared per gram. Table 3-21 presents the average properties and variances of the eight specimen groups. The specimens were in the form of thin (0.35 mm) discs, approximately 2.5 cm in diameter. Density was measured by the Archimedes method. Strength was measured in a biaxial mode using an Instron mechanical testing machine. The disc specimens were supported on three steel balls and were mechanically loaded from the top through an alumina rod. The crosshead speed during the mechanical loading was 0.13 cm/min. Elastic modulus and Poisson's ratio were evaluated by sound velocity measurements using the pulse-echo technique.

B-26923

Figure 3-72. Weibull Failure Probability Distributions of Strength Data for $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Interconnect Specimens

TABLE 3-20				
IDENTIFICATION AND PROCESSING VARIABLES FOR ELECTROLYTE SPECIMENS				
Sample Group	No. of Specimens	Particle Size	Solid Loading	Sintering Temp, °C
EC037-101 to 126	19	Coarse	55 vol. %	1100
EC038-127 to 150	24	Coarse	55 vol. %	1400
EC037-001 to 025	21	Coarse	45 vol. %	1100
EC038-026 to 050	23	Coarse	45 vol. %	1400
EC061-176 to 200	19	Fine	55 vol. %	1100
EC060-151 to 175	23	Fine	55 vol. %	1400
EC061-076 to 100	22	Fine	45 vol. %	1100
EC060-051 to 075	24	Fine	45 vol. %	1400

TABLE 3-21				
MEASURED PROPERTIES OF ELECTROLYTE SPECIMENS				
Sample Group	Density, g/cc	Elastic Modulus, GPa	Poisson's Ratio	Strength, MPa
EC037-101 to 126	3.70 ± 0.02	34.2 ± 6.4	0.24 ± 0.02	24.8 ± 6.6
EC038-127 to 150	5.91 ± 0.07	252.6 ± 42	0.33 ± 0.02	149.8 ± 41.2
EC037-001 to 025	3.46 ± 0.02	23.1 ± 0.5	0.27 ± 0.01	16.9 ± 3.0
EC038-026 to 050	5.89 ± 0.05	249.4 ± 3.3	0.31 ± 0.02	107.4 ± 35.6
EC061-176 to 200	3.71 ± 0.03	57.3 ± 2.2	0.27 ± 0.02	34.2 ± 10.3
EC060-151 to 175	6.01 ± 0.02	255.3 ± 4.8	0.31 ± 0.02	150.9 ± 31.9
EC061-076 to 100	3.35 ± 0.02	30.5 ± 1.6	0.23 ± 0.003	20.7 ± 3.8
EC060-051 to 075	5.94 ± 0.03	267.6 ± 5.8	0.31 ± 0.01	114.2 ± 27.5

The most significant finding was that the electrolyte strength was a strong function of the solids loading. At the 1400°C sintering temperature the higher solids loading (55 percent) resulted in approximately a 40-percent increase in strength over the lower solids loading (45 percent). The Weibull modulus, m , calculated from the slopes of the linear regression lines, showed values in the range of 3.21 to 6.79, suggesting a large scatter in strength data for all specimen sets. Slightly higher density and strength were

achieved with the fine particle size vs the coarse particle size. The 1100°C sintering temperature was obviously too low to achieve usable electrolyte material, but showed similar trends.

3.6 ANCILLARY MATERIALS DEVELOPMENT

In this task the sealant technology developed at ANL was applied to the MSOFC. The work was divided into several activities including: (1) bonding tests, (2) thermal cycling tests, (3) sealant property modifications, and (4) sealant/SOFC materials interactions.

3.6.1 Bonding Tests

As a first step, identical substrates were bonded together into symmetric sandwiches (e.g., cathode/sealant/cathode) as shown schematically in Figure 3-73. The paste used in the experiments consisted of 1 g of Material K and 0.36 g of glycerol. The ceramic materials used are given in Table 3-22; all are about 4 to 5 mm wide and 0.6 mm thick. Pieces about 10 to 25 mm in length were used in the experiments described below.

Figure 3-73. Schematics of Structures Sealed with Material K.
In All Drawings, Sealant Layer is Represented as Colorless.

TABLE 3-22	
MATERIALS USED IN EXPERIMENTS	
Material	Lot
Cathode	CE-0507303
Anode	A-506
Electrolyte	None
Interconnect	I-04263-1

After spreading a thin layer of the sealant on the ceramic substrates and assembling the sandwiches, the samples were fired on a bed of yttria-stabilized zirconia (YSZ) powder to minimize interaction with the Al_2O_3 setter. They were heated to 1000°C over 3.5 hr, held at 1000°C for 6 hr, and then cooled to room temperature in 3.5 hr.

After firing, the samples were examined under low magnification (3X) for signs of bonding and gross interactions. In all cases, the sealant wet the substrates well and formed strong bonds. Some observations are given in Table 3-23. After seven to eight thermal cycles between room temperature and 800°C in air, no cracking was seen.

TABLE 3-23	
OBSERVATIONS ON CERAMIC/SEALANT/CERAMIC SANDWICHES	
Sample	Observations
I/sealant/I	Sealant has a greenish cast (Cr diffusion?)
C/sealant/C	Sealant has a brownish cast (Mn diffusion?)
A/sealant/A	Sealant is off-white

As a next step, the sealing behavior of Material K was tested in a more complex geometry. Here, the sealant had to bind to and tolerate the thermal behavior of three different ceramics simultaneously. The channel ceramics consisted of interconnect/cathode/electrolyte (I/C/E) and interconnect/anode/electrolyte (I/A/E). The channels were about 2 to 4 mm deep. The sealant paste consisted of 1 g of Material K blended with approximately 0.28 g of DMF. The channels were temporarily held together with Apiezon T grease while the paste was put in the channel with a spatula. In all, four of each type of channel were made. They were fired as described above. After firing, they were thermally cycled between room temperature and 1000°C using heating and cooling rates of $4^\circ\text{C}/\text{min}$ with a 6-min hold at 1000°C . Again, they were fired on a bed of YSZ powder to minimize interaction with the Al_2O_3 setter. The sealing step was not counted as a thermal cycle.

After each cycle, the samples were examined visually or under 10X magnification for signs of cracking. For the first four cycles, no change in any samples was evident. After the fourth cycle, some signs of wicking of sealant into an I/C/E sandwich were seen. The sandwich was removed from further cycling and awaits examination. The test was continued until a total of seven cycles was completed. No obvious signs of cracking in the sealant or substrates were seen. These samples will be examined more fully later.

Finally, the angle structure, shown in Figure 3-73, was fabricated to simulate how the manifolding (YSZ) would be attached to the stack at either an YSZ layer or an interconnect layer. Note that the structure was assembled in this first test in the configuration shown in Figure 3-73; that is, the horizontal member was at the bottom, not the top (as would be found in the actual joint). Two structures were made; one contained YSZ

as the angled member, and the other, interconnect. The horizontal member was YSZ in both cases.

The effect of a higher sealing temperature was also investigated. The sealing temperature was raised to about 1025°C, and the remainder of the thermal profile was held constant.

The paste was made as described above with 1 g of Material K to about 0.28 g of DMF. A bead of the paste was made along the midline of the horizontal member using a spatula, and the angled member was placed in the bead. The angled member was supported externally by a calcia-stabilized ZrO₂ block.

After the sealing step, the angles were examined using an optical microscope (10X magnification). In both structures, the sealant was found to wet all sealing surfaces well and formed strong bonds. Additionally, a few closed, hairline cracks were observed on the acute-angle side of these structures. On the obtuse-angle side, the sealant had a globular appearance which is probably due to the crude method of application.

Present work, and that planned for the near future, is focused on sealing electrolyte and interconnect materials, as would be needed for sealing the test fixture and manifold.

3.6.2 Thermal Cycling Tests

A important property of a sealant is its ability to be thermally cyclable. The sealant should not crack, nor should it cause the cracking of bound substrates. Cell geometry will also be a factor in determining the stresses that the sealant must tolerate.

To this end, composite structures consisting of interconnect/cathode/electrolyte and interconnect/anode/electrolyte (four each) were arranged to form a channel, as shown schematically in Figure 3-74, and sealed with Material K. The stresses developed due to thermal expansion mismatch in the structure are close to those found at the cell edge. The sealed channel was about 4.5 mm wide, 3 to 4 mm long, and 0.5 to 0.6 mm thick.

B-28283

Figure 3-74. Schematic of Arrangement of Bonded Ceramics Used in Thermal Cycling Tests

Two tests were performed: one cycling both types of structures in air between room temperature and 1000°C, and the other cycling the anode-containing structure under humidified, 5 percent H₂/He. In both cases, the time at 1000°C was kept to a minimum. The heating and cooling rates in the former test were 3°C/min each, and in the latter about 8°C/min for heating and about 1°C/min for cooling (natural furnace cooling). The samples were examined periodically using an optical microscope. One sample in each test failed during cycling; this is ascribed to fabrication flaws.

After seven thermal cycles in air, the test was voluntarily stopped. No cracks were seen in any of the samples. All samples appeared to be well wet by the sealant. As observed before, some discoloration of the sealant adjacent to the cathode was seen. A brown layer was present and is believed to be due to the migration of Mn into the sealant. It is not yet known whether this process is detrimental to cell performance.

Ten thermal cycles were accumulated on the test in 5% H₂ in He. No cracking was seen in any of the samples. The sealant wet the interconnect and electrolyte well. On two of the three samples, the sealant wet the anode fairly well. A close inspection of the third sample showed that the sealant did not come into contact with the sample.

The samples are undergoing further examination and analyses.

3.6.3 Sealant Property Modifications

Manifold sealing tests indicated that Material K did not flow sufficiently at 1000°C in sealant tests (see fabrication section).

The observation was that spaces were formed between beads of sealant. Thus, either the surface tension of the sealant at temperature was too high or its viscosity was too high. Altering the composition of the sealant is being used as a means to modify the two physical properties.

Three compositions were made with 5, 10, and 20 wt% glass additions. Pastes of the new materials were used to test the sealing of the interconnect to the electrolyte at 1000°C. After firing, each modified composition formed smooth seals at the ceramic junction. Examination of these joints under the optical microscope revealed that the best seal was that formed by using the material containing the 10 wt% glass addition. A sample of this material has been evaluated for stack sealant applications.

3.6.4 Sealant/SOFC Materials Interactions

A study to examine the interactions of the developed sealant with the different SOFC materials has continued. To date, samples of component/sealant have been held in an oxidizing environment at both 800°C and 1000°C for times ranging from 24 to 500 hr.

In the first portion of this work, anode, cathode, electrolyte, and interconnect materials were contacted with small beads of premelted sealant at 1000°C in air for periods of 24 to 124 hr. Because the heating/cooling schedule was reported in the previous

monthly report, it has not been repeated here. Samples taken after 24, 74, and 124 hr were examined by optical microscopy; these results are summarized below.

In the second portion of this work, the SOFC materials were contacted with sealant paste. The use of the paste decreased the amount of sealant per sample to a level typical of that expected in stack assembly. Bonding of the substrate/sealant was made by heating the samples at 180°C/hr to 1000°C and holding at temperature for 6 hr; a similar cooling rate was used. This bonding process generally caused the material in the sealant paste to coalesce into bead-like shapes on the substrate. This was true irrespective of the composition of the substrate. At times, the beads were joined by a thin layer of sealant; at others, the beads were isolated from each other. These beads were considerably smaller than those used in the first portion of this work. Sixteen samples (four sets of each component) were prepared for use in this portion of the study. One set was kept for reference/baseline studies.

Three sets of samples consisting of component/sealant were heated to 800°C at a rate of 3°C/min, held for the desired time, cooled to 200°C at a rate of 3.3°C/min, and then brought to room temperature with the furnace switched off. Samples of component/sealant taken at 1 hr and one thermal cycle, 300 hr and two thermal cycles, and 500 hr and three thermal cycles were examined by optical microscopy; these results are also summarized below.

(a) Anode/Sealant Bead — 1000°C

A glass-wet region encircled each sealant bead and, because of the excess of sealant, the substrate was also wet through its depth with glass. The initial bonding at 24 hr looked good. However, after 124 hr at temperature, the interface between the sealant and anode looked porous, and the sealant bead was easily removed from the substrate. Examination of the sealant showed that the bead was very porous, with little of the glassy portion remaining.

(b) Anode/Sealant Paste — 800°C

There appeared to be little difference between the baseline sample and one held at temperature for 500 hr. The substrate/sealant bond looked good, and the interface texture was similar. The penetration of the glassy phase into the substrate appeared to be related to the bead size, as might be expected. There was no visual evidence of a porous layer as seen with the long-term high-temperature sample reported above.

(c) Electrolyte/Sealant Bead — 1000°C

The bonds looked good and unchanged with time at temperature. The sealant bead could not be removed from the substrate, even after 124 hr at temperature.

(d) Electrolyte/Sealant Paste — 800°C

The bonds looked good and appeared to be unchanged by time at temperature. They were similar to those formed in the long-term high-temperature samples. One minor difference is that the sealant beads in the 800°C samples tended to lose their glassy look with time. This may be evidence that the glassy portion of the bead continues to flow with time.

(e) Cathode/Sealant Bead — 1000°C

Early bonding (≤ 24 hr) looked good. The sealant showed signs of Mn migration, which intensified with time at temperature. A solid ring of dark material formed about 2 mm from the sealant/cathode interface in the sample held at temperature for 124 hr. It is suspected that this ring is rich in manganese, but has not been able to substantiate this. The sealant bead was well bonded to the substrate, even after 124 hr at temperature, and though the bead was removed from the cathode, it did not separate readily.

(f) Cathode/Sealant Paste — 800°C

The sealant/cathode bond looked good even after 500 hr at temperature. As with the electrolyte, the sealant lost its glassy appearance with time. In these samples, the sealant showed evidence of Mn migration, and specks of dark material formed and concentrated on the surface of the sealant; the number of specks increased with time at temperature.

(g) Interconnect/Sealant Bead — 1000°C

In general, the bonds looked good irrespective of the time at temperature; however, the sealant bead was easily removed from the substrate of the 124-hr sample. There was evidence of Cr migration in all the samples, with the Cr concentration in the sealant increasing with the time at temperature. In addition, the samples held at temperature for 74 and 124 hr cracked in the region below the bead. The cracks appeared to result from thermal cycling and the differences in thermal expansion between the sealant and the substrate.

(h) Interconnect/Sealant Paste — 1000°C

The bond between the sealant and the substrate looked good for all the samples. However, there was a change, with time, in the appearance of the glass-wet region that surrounded the sealant bead. This change involved what appeared to be a decrease in the glass-wet region, and an increase in the size of crystals in the substrate below the glassy region. All of these samples survived thermal cycling without any evidence of cracking. As in the higher-temperature study, there was evidence of Cr migration increasing with time at temperature,

(i) Summary of Materials Interactions

Several preliminary conclusions can be drawn about the interactions of the sealant and the substrates at the two temperatures investigated. These are as follows:

- (1) A short time at 1000°C results in good bonding between the sealant and the substrate.
- (2) Both Cr and Mn migrate from the substrate even at 800°C, and the amount will depend on the time at temperature.
- (3) The component/sealant will thermally cycle at 800°C without deleterious effects.
- (4) The interaction of the interconnect with the glassy portion of the sealant needs to be studied more extensively.

4. FABRICATION

The ultimate objective of monolithic solid oxide fuel cell (MSOFC) development is to create a product that can be manufactured in a single thermal processing cycle and configured such that the anode/electrolyte/cathode (A/E/C) trilayer is corrugated and manifolded in a coflow configuration. The former attribute reduces the costs of stack processing, and the latter increases the achievable power density of the MSOFC, reducing material costs. However, the technical challenges associated with developing the associated technology are significant. Because of the anticipated difficulties in manifolding a corrugated coflow MSOFC, a crossflow approach with planar cell and corrugated electrode configuration was selected as the baseline construction at program inception.

The materials issues encountered are discussed in Section 3. Early in the project it was recognized that developing an interconnect that could be fired simultaneously with the electrodes would be a difficult and time-consuming task. Although a significant effort was undertaken to develop a cofired interconnect, an alternative approach was undertaken to cofire single cells with electrode corrugates and bond them with sintered interconnects. Although this approach proved successful at small scale, at footprints larger than approximately 2 in. by 2 in. the yield of the cofired assemblies was very low. Subsequently, an approach involving the bonding of sintered cells, electrode bars, and interconnect plates was adopted, and this was the baseline for scaled fabrication.

During the course of this project ASE developed thin-film electrolyte cell technology. This process involves sequentially rolling bilayer tapes of anode and electrolyte in such a manner that the electrolyte layer is ultra-thin. The bilayer is then cofired, a cathode slurry is applied to the bilayer, and the cell is fired. In this manner uniform electrolyte layers as thin as 1 micrometer can be formed. This construction technique leads to cells which exhibit the best performance of all known fuel cells. At 1000°C a power density of 900 mw/sq cm has been achieved. It was demonstrated that the cells fabricated in this manner can be scaled to an area of 500 sq cm with high fabrication yield. These cells were used in the plate and bar stack construction.

The task was to culminate in the fabrication of a 100-w stack. Although several manifolded stacks were built which had the potential (based on single-cell performance and stack resistivity analysis) to achieve 100 w, the tests were not successful.

However, with a combination of good component thermal expansion matching and stack designs which minimized component stresses, stacks were fabricated which could be thermally cycled in air with no evidence of performance-compromising damage. Due to difficulties with hydrogen compatibility of the lanthanum chromite interconnect material and the lack of a suitable sealant, significant stack defects occurred upon the introduction of hydrogen to the fuel cell. These defects were sufficient to cause the performance-shortfalls exhibited by the stacks.

4.1 BASIC PROCESSING TECHNOLOGY FOR FABRICATION OF CELLS AND STACKS

MSOFC cells and stacks in this program were fabricated using a fabrication sequence based on the tape calendering technique.

The tape calendering process involves laminating several individual tape layers together by passing them between the rolls of a two-roll mill. The laminated tape is then thinned by decreasing the spacing between the rolls and passing the tape successively through the mill until the desired thickness is achieved. The tapes used in the study consist of ceramic powders incorporated in a binder/plasticizer system. This incorporation takes place when the ceramic powders along with the binder (which is added in a powder form) and plasticizer are placed in a high-intensity mixer and mixed while heating. The heat softens the binder/plasticizer system, allowing the resulting plastic mass to be rolled into the individual tapes. This process is depicted in Figure 4-1. These tapes are flexible and can be thinned to the desired thickness as described.

After the tapes are laminated and the appropriate thickness is achieved, single cell discs and other single or multilayer discs can be made from the tape. The discs are cut ultrasonically to a selected diameter. The tapes can also be compression molded into the corrugations that compose the MSOFC stack designs. After molding, a flat layer of laminated tape is bonded along the top of the corrugations of the molded tape to create a layer of enclosed gas chambers. After the bond between the flat and corrugated layers has dried, the assembly can be cut to the desired size, and the layers are bonded on top of one another to build the desired stack height. The stacking of the layers also encloses the gas chambers on the other side of the molded corrugation, thus completing the MSOFC design. Figure 4-2 is a representation of this process. This process can be used to fabricate either coflow or crossflow MSOFC designs. The only difference is in the type of tapes used for compression molding and for the flat cover sheet. For the coflow design, laminated tapes containing the electrolyte layer are molded and the flat layers of the stack include the interconnect layer. The crossflow design requires only monolayer electrode tapes to be molded while the flat layer of the stack contains alternately the electrolyte and interconnect layers.

The overall fabrication scheme based on the tape calendering technique is shown in Figure 4-3. Figures 4-4 to 4-6 show the details of the mixing, rolling and laminating, and corrugating steps of this fabrication sequence.

4.1.1 Cell Fabrication

In the early stages of the program, cells were formed by laminating the anode, electrolyte, and cathode tapes together and cofiring them. Extensive efforts were made to ensure that the overall shrinkage and the shrinkage and sintering dynamics of each of the components during thermal processing were closely matched. Additionally, the effects of thermal expansion mismatches of the components were evaluated via analysis of the stresses induced during the cool-down portion of the thermal processing cycle following sintering. This was done to minimize warpage, fracturing, and delamination of the cells. During thermal processing, setter plates were used to physically

Figure 4-1. Representation of the Batching, Calendering, and Lamination Process for Fabricating Monolithic Solid Oxide Fuel Cells

Figure 4-2. Representation of the Compression Molding and Stacking Process for Fabricating Monolithic Solid Oxide Fuel Cells

A-92568-A

Figure 4-3. Fabrication Scheme Based on Calendering Technique

F-55969

Figure 4-4. High-Intensity Mixer is Used to Prepare a Homogeneous Mixture

F-55968

Figure 4-5. Rolling of Individual Ceramic Tapes and Trilayer Tapes in a Two-Roll Mill

F-55966

Figure 4-6. Corrugation of MSOFC Tapes by Compression Molding

constrain the cells to ensure that the fired cells were as flat as possible. The cells constructed during this project were typically approximately 250 micrometers in thickness.

Initially, based on empirical results, the cell construction was chosen to have the thickness ratios of 1:5:1 for the anode:electrolyte:cathode layers. Later, based on the results of modeling the stress induced in component layers by various cell constructions, a cell thickness ratio of 2:1:1 was chosen. This construction proved to produce more robust sintered cells. However, as the footprint of the cells increased the cell yield decreased. Cells of a 4-in. by 4-in. footprint were fabricated with very low yield.

Eventually, the electrochemical performance advantages of the thin-film electrolyte technology became evident. In this processing approach, shown in Figure 4-7, a bilayer is formed from a thick anode and thin electrolyte tape. Subsequently, anode tape is co-rolled with the bilayer and the process is repeated until the desired electrolyte thickness is achieved. In this manner electrolyte layers as thin as 1 micrometer can be formed on the anode substrate (see Figure 4-8).

The bilayer is then fired (see Figure 4-9), the cathode slurry is applied, and the trilayer is fired. Figure 4-10 shows a fracture surface of the thin-electrolyte cell with porous cathode and anode and dense electrolyte.

Additionally, it was found that cells fabricated in this manner were scalable and extremely robust. Cells with footprints up to 500 sq cm in area with no performance-compromising defects are routinely produced with nearly 100-percent yield. The process is easily adaptable for making cells of multilayer construction (having more than three layers) or cells from tapes having different rolling characteristics.

4.1.2 Stack Fabrication

As discussed above, the MSOFC concept in its preferred embodiment requires only one thermal processing cycle. However, a suitable interconnect was not found, and an alternative approach was implemented. This approach involves firing components and component assemblies individually and then assembling and bonding them. This approach is called "two-step cofiring."

4.1.2.1 Stack Fabrication With Single-Cell Modules and Stacks

The initial attempts at stacking involved forming green state single-cell modules and "stacks," and cofiring these assemblies. The single cell module comprises flat-plate anode/electrolyte/cathode (A/E/C) with cathode and anode corrugates attached to the cathode and anode of the A/E/C flat plates (see Figure 4-11).

A single-cell stack consists of a single-cell module with a cathode plate attached to the cathode corrugate and an anode flat plate attached to the anode corrugates (see Figure 4-12).

B-27068

Figure 4-7. Fabrication Sequence

Figure 4-8. Thin-Electrolyte/Anode Bilayer Formed by Tape Calendering

Figure 4-9. Sintered Bilayers

Figure 4-10. Fracture Surface of Thin-Electrolyte Cell

Figure 4-11. Single-Cell Module Construction

IG-12436

Figure 4-12. Single-Cell Stack Construction

Interconnect plates are formed and fired separately. The interconnect plates are then assembled with a bonding agent to the modules or single-cell stacks and the assembly is formed into a multicell stack and fired (see Figure 4-13).

4.1.2.1.1 Single Cell Module Fabrication

Early in the project numerous cofired single-cell modules were fabricated to gain experience with the cofiring process, assess the physical defects associated with fabrication, and provide "building blocks" for two-cell stacks.

In forming the two-cell stacks from modules it was found that it was quite important to maintain flat and parallel surfaces on the top and bottom to form good bonds with the interconnect plates. A great deal of effort was directed at decreasing the amount of bowing that occurs during module processing. Bowing in the plane of the anode channels resulted in a small convex curvature when viewing the anode surface of the stack. Bowing was slightly more severe parallel to the anode channels than perpendicular to them. Investigation of top constraint weight during processing of the 2-in. (green state) footprint modules revealed that approximately 115 g was the upper limit for avoiding excessive corrugation collapse. Stack orientation during processing was found to affect the degree of bowing. When larger constraint weights are used, processing, with the anode surface up, results in less bowing. Most of the modules processed had a 5-cm square green footprint. Modules possessing larger green footprints

Figure 4-13. Two-Step MSOFC Assembly

IG-12384

of 6.25 and 7.5 cm were successfully processed and reproduced. These modules had approximately 5.25 and 6.25-cm footprints after processing.

Since unacceptable bowing occurred even with the largest possible constraint weights, efforts were made to modify module constituents to further decrease bowing. The objective of the modifications was to improve shrinkage matching and thereby lessen the amount of stress present during thermal processing. Anode batches of 50-vol% solids loading, A07030, and 47-vol% solids loading, A07300, were used as the first iteration in investigating module constituent modification.

When batch A07030 (50 vol%) was made, it was incorporated into modules as the anode within the 1:5:1 flat layer and as the corrugated layer. The first two firing runs with these modules resulted in 5 of 16 uncracked modules. These runs utilized baseline processing variables. This yield was far below that of previous modules processed using baseline variables and composition. Batch A07300 (47 vol%) was then made and incorporated into modules as the anode within the 1:5:1 layer and as the corrugation. When these modules were processed using the baseline variables, the yield was 1 of 6. Within the same run, two modules that contained A07030 (50 vol%) with a lesser top constraint weight were both successfully processed. Based on this result, a test was set up for processing modules, incorporating A07030 and A07300 separately and in combination with a lesser top constraint. Table 4-1 is the matrix for this test. All modules were processed without visible cracking. Inspection showed that ST1252 and ST1253 exhibited the least amount of bowing among the modules in the test. Table 4-1 shows that these modules have A07300 (47 vol%) as the corrugation and A07030 (50 vol%) within the 1:5:1. In order to verify this result, another test consisting of four modules similar to ST1252 and ST1253 and four modules containing A07300 (47 vol%) in both the corrugation and 1:5:1 was performed. This test confirmed the results obtained with modules ST1252 through ST1259. A low-energy dispersive X-ray analysis, as described in the March 1990 quarterly report, ASE Document 90-63592(3), pages 3-2 and 3-3, revealed cracks that were presumably within the middle 1:5:1 layer in the modules fully comprised of A07300 (47 vol%), while no cracks were discovered in the modules containing A07300 and A07030.

Initially, module bowing was evaluated by visual inspection or measurement with a height gage. These methods are time-consuming and do not always provide consistent results. A new method using an optical comparator in the surface reflectance mode was developed. This method is quicker and less operator dependent than the visual and height gage methods. The optical comparator reflects a light beam off of the surface of the sample and transmits the shadow of the surface profile onto a screen that is marked with crosshairs. The contour of a sample can then be measured digitally by moving the sample with a joystick so the shadow moves across the screen. By placing the module onto a flat table, the gap between the top surface of the table and the bottom surface of the module can be measured. Measurements are taken along the side of the module at six specific locations corresponding to some of the corrugations. Each of the four sides of the module are measured. The average gap and average standard deviation of the gap is calculated for each module. Examples of such

TABLE 4-1		
TEST MATRIX FOR EVALUATING MODULE CONSTITUENTS WITH LESSER TOP CONSTRAINT WEIGHT		
Stack Number	Corrugation Anode	1:5:1 Cell Anode
ST1252	47v%	50v%
ST1253	47v%	50v%
ST1254	47v%	47v%
ST1255	47v%	47v%
ST1256	50v%	50v%
ST1257	50v%	50v%
ST1258	50v%	47v%
ST1259	50v%	47v%
Key: 50 vol% - A07030 47 vol% - A07300		

measurements and calculations are shown in Table 4-2. The column headed "CORR. U or D" refers to the position of the corrugations for the side being measured. The averages for the modules are shown below the calculated average and standard deviation for each side. Optical comparator measurements will allow the evaluation of modifications to the construction and processing of modules. Also, these measurements enable the implementation of go/no-go criteria for incorporation of modules into the second step of the two-step cofiring process.

TABLE 4-2												
OPTICAL COMPARATOR MEASUREMENTS AND CALCULATED AVERAGES FOR ST1252 AND ST1253												
Stack No.	Side	Corr. U or D	1	4	7	10	11	14	17	20	Average	STD. Dev.
ST1252	1	D	0.0052	0.0060	0.0045	0.0000	0.0000	0.0038	0.0064	0.0030	0.0036	0.0025
	2	U	0.0000	0.0052	0.0071	0.0086	0.0086	0.0069	0.0070	0.0048	0.0060	0.0028
	3	D	0.0027	0.0040	0.0026	0.0019	0.0019	0.0027	0.0037	0.0019	0.0027	0.0008
	4	U	0.0030	0.0059	0.0064	0.0067	0.0074	0.0085	0.0080	0.0034	0.0062	0.0020
ST1253											0.0046	0.0020
	1	D	0.0045	0.0042	0.0022	0.0015	0.0015	0.0028	0.0067	0.0045	0.0035	0.0018
	2	U	0.0042	0.0064	0.0073	0.0074	0.0073	0.0097	0.0115	0.0054	0.0074	0.0023
	3	D	0.0015	0.0074	0.0035	0.0020	0.0020	0.0020	0.0063	0.0040	0.0036	0.0022
	4	U	0.0045	0.0085	0.0086	0.0084	0.0084	0.0064	0.0064	0.0000	0.0064	0.0030
											0.0052	0.0023

Further efforts to reduce bowing and to reduce defects in single-cell modules concentrated on changes in the thickness ratios in the cell trilayer. Analysis showed that a 2:1:1 A/E/C ratio would produce modules with reduced component stress incurred during the cool-down portion of the thermal processing cycle when compared to the baseline 1:5:1 construction.

Both 2:1:1 and 1:5:1 trilayers were evaluated with green footprints of 2.0-, 2.5-, and 3.0-in. square. SEM analysis of sintered 2.0-in. (green dimension) 1:5:1 modules revealed defects at both electrode corrugation/trilayer interfaces like those shown in Figure 4-14. No defects were found upon SEM analysis of the 2.0-in. green 2:1:1 modules. For both ratios, bowing was convex when the module is inspected from a view looking along the CE channels and the module's anode side is facing up. The 2:1:1 modules had a lesser degree of bowing than the 1:5:1 modules. Figure 4-15 shows the results of the 3.0-in. green 1:5:1 and 2:1:1 modules. Results were the same with the 2.5-in. modules. No defects were detected in the 2:1:1 modules during a 70x optical inspection. The degree of bowing did increase with footprint; however, the difference between 2.5- and 3.0-in. seems to be greater than that between 2.0- and 2.5-in. The results of the 2:1:1 modules with all three green footprints have been reproduced. Figure 4-16 shows all three footprint sizes after firing.

Figure 4-14. SEM Micrographs of Typical Crack in 1:5:1 Single-Cell Module EE170-01

Based on the results of this experimental investigation all subsequent fabrication of single-cell modules was based on the 2:1:1 construction.

An optical comparator was used to establish the average gap of modules containing baseline batches with 2:1:1 A:E:CE thickness ratio. The range of the average gap of the modules measured was 8.0 to 11.0 mils.

F-60259

F-60260

Figure 4-15. Processing Results of EE173-01 3.0-in. Green 1:5:1 Single-Cell Module (Right) and EE173-02 3.0-in. Green 2:1:1 Single-Cell Module (Left)

F-60261

Figure 4-16. 2:1:1 Single-Cell Modules with Green Footprints (from Left to Right) of 3.0, 2.5, and 2.0 in.

F-60262

Sintered modules were examined for the presence of defects using the simplified classification system. The type of defect and its occurrence in more than 100 modules fabricated are given in Table 4-3.

TABLE 4-3		
DEFECTS IN SINTERED SINGLE-CELL MODULES		
Category	Description	Occurrence, percentage
I	No defect found	35.7
II	Defect (hairline crack) barely identifiable at 70X and not found within electrolyte layer	22.4
III	Defect (hairline crack) easily identifiable 70X and not found within electrolyte layer	18.4
IV	Defect (hairline crack) found in or through electrolyte layer	15.3
V	Macroscopic crack or fracture	8.2

Category I and II modules were selected for further use in fabricating testable multicell stacks by the two-step, cofiring process. Category III and IV modules were used for developing second-step bonding processes.

Several modifications to module fabrication and processing were implemented. Fabrication modifications involved modification of the compression molding procedure and green-state roughening of intermediate corrugations. The purpose for modifying the compression molding procedure was to further improve corrugation uniformity, resulting in less corrugation slumping during processing. The refinement was to modify the tooling to increase die alignment along the corrugation channels during molding. The result was an observed increase in green-state corrugation uniformity.

Green-state roughening of the intermediate corrugations was attempted to induce texture and increase bond area in modules for improved bonding at intermediate interfaces. Roughening was performed on corrugated tapes by softening the binder and then placing a rough surface in contact with the corrugation peaks. This modification has provided a surface that is more conducive to second-step bonding at interfaces involving intermediate corrugations without any discernible effect on module processability. Figure 4-17 shows unroughened and roughened intermediate corrugations on modules that have been sintered. Roughening is now routinely applied to all cathode corrugations used for module fabrication.

Processing modifications involved altering module orientation in the furnace and reducing the top constraint weight. The purpose of altering module orientation in the furnace was to obtain a cleaner corrugation surface after sintering and to minimize defects. Cleaner corrugation surfaces improve second-step bond strength. The surface

F-64186

Figure 4-17. Unroughened (left) and Roughened (right) CE Corrugation Surfaces in Sintered Single-Cell Modules

in contact with the bottom setter was changed from intermediate corrugation to anode corrugation. This modification resulted in a lower number of Category V modules; i.e., macroscopically fractured. Reducing the top constraint weight was done to alleviate the corrugation slumping during processing. Top constraint weight was halved, and resulting modules were evaluated for corrugation form, flatness, and defect types (listed in Table 4-3). No slumping was observed since corrugations retained their green-state form. Optical comparator measurements revealed only a 1-mil increase in range of the average gap. This range is still lower than that considered an acceptable flatness value. There was no discernible change in the occurrence of defect types as a result of halving the top constraint weight.

It is desirable to have sintered modules as flat as possible for bonding in the two-step, cofiring process. As previously mentioned, the average gap (flatness) on baseline modules is 8.0 to 11.0 mils. One way to decrease the average gap is to use more top constraint weight during green-state processing. However, added weight increases the likelihood of corrugation slumping and higher category defects. Creep flattening was evaluated as a way of increasing module flatness. A creep-flattening experiment was carried out at 1350°C with several levels of constraint weight: 0 (unconstrained), 1/3 max., 2/3 max., and max. The experiment used Category II modules. In

all four cases, the Type II defects in these modules widened or propagated to become Type III defects. An example of the resulting Type III defects is shown in Figure 4-18. The constrained modules were flatter by varying degree. The unconstrained module showed significant bowing, indicating further sintering of the sample at the experiment temperature. Whether defects would be initiated in Category I (defect-free) modules is unknown at this time.

F-64188

Figure 4-18. Type III Defects Observed at CE Corrugation/Trilayer Interface of Single-Cell Module After Creep Flattening

To obtain flat stacks with well-defined gas channels, varying the constraint weight during processing was attempted; low weight was used for low-temperature binder extraction and high weight was used for the sintering temperature regime. This variation can be performed by splitting the processing run into two steps. In the first step, the green sample is constrained with a low weight and fired to a temperature lower than sintering temperature but higher than binder burnout temperatures. The sample can then support more weight. In the second step, the sample is then fired to the sintering temperature with a higher constraint weight. This higher load assists in flattening the sample during sintering, a type of creep-assisted sintering. Two maximum temperatures were investigated for the first step. The first, 600°C, is just above the binder burnout temperature, while the other, 1300°C in the first step proved better because the resulting stacks had fewer defects. The constraint weight used in the second step is double that used in the first step. This creep-sintering process has yielded flat modules and electrode-covered modules with minimal observable defects.

A study was carried out to determine the most suitable building block for the two-step bonding process.

Several matrix experiments were designed and performed to determine stack geometry and processing parameters for a given batch combination to produce building blocks with minimal defect count. The experiments covered several batch combination and stack geometry variables. The variables on batch combination included standard and high solid loading A and standard and alumina-modified CE. The variables on stack geometry were single cell module, electrode-covered module, and single cell stack. Samples were processed via standard firing process or the creep-sintering process. Sintered samples were judged on defect type and frequency, flatness, and process throughput.

The results of the experiments indicated that single cell stacks possessed the highest defect frequency while the single cell modules had the lowest. The defect type and frequency of the electrode-covered modules depended on batch combinations. In general, single cell modules composed of baseline anode, electrolyte, and cathode/electrolyte intermediate were superior in all categories. These samples possessed a type I yield over 90 percent and a gap of approximately 4 mils as measured on the optical comparator. This measured gap also represents a 33 percent decrease in degree of bowing compared to modules fabricated during the two previous quarters. Furthermore, the throughput was highest for single cell modules. This high throughput could be obtained for modules by the standard firing process rather than the more complex creep-sintering process necessary for electrode-covered modules and single-cell stacks.

Based on these results, the single-cell modules were selected over the single-cell stacks as the fundamental building blocks for small-scale stack fabrication.

4.1.2.1.2 Single Cell Stack Fabrication

Evolution of fabrication of the single-cell stacks proceeded along similar lines to that for the single-cell modules. There were basically two processes for fabricating single-cell stacks. The first method was to cofire the green state assembly. The second method, used primarily to evaluate bonding technology, was to bond flat anode and cathode plates to the processed single-cell modules.

Early in the project cofired single-cell stacks with green-state footprints of 1.3 in. and 2.0 in. were fabricated. Major cracking throughout the stack occurred in the larger footprint stacks while the smaller footprint stacks exhibited narrow cracking in the electrode cover sheets and within the single cell layer. Figure 4-19 shows typical crack patterns for both footprints. Narrow cracks in stacks are attributed to thermal expansion coefficient (TEC) mismatch. In an effort to alleviate this problem in the smaller footprint stacks, some processing modifications were attempted. The first modification was to cut the cooling rate in half. This was expected to reduce the effects of the stress caused by TEC mismatch. The other modification was to combine the lower cooling rate with altering the sample setter. The setter change was imbedding the sample in coarse zirconia powder. The powder would then act as a radiation shield to provide

Figure 4-19. Photograph of (a) ST1311, 1.3-in. Green Footprint, and (b) ST1312, Possessing 2.0-in. Green Footprint Showing Typical Crack Patterns

more uniform temperature distribution during firing. First attempts with these processing modifications showed that the slower cooldown did help prevent narrow cracks from occurring in the electrode cover sheets, but some cracking in the 1:5:1 single cell layer was still present. Results from imbedding a stack in coarse zirconia powder were difficult to assess as some powder imbedded into the channels of the stack.

Using the results of the stress analysis model, the effects of the A:E:C layer thickness ratio on the processing of single cells and single-cell stacks were investigated. Single cells and single-cell stacks were fabricated with relative thickness ratios (A:E:C) of 1:1:1, 2:1:1, and 1:5:1. Concurrently, attritor milled NiO was compared with ball-milled NiO in the anode layer. The processing behavior and the types of defects were examined for each cell construction.

Single cells and single-cell stacks were fabricated from material of batches A03221-1, A02101-1, E03221-1, and CE03231-1. Batch A03221-1 is an anode batch incorporating NiO, which was attritor-milled (AM) to obtain the target surface area. Batch A02101-1 is an anode batch in which the NiO was ball-milled (BM) to obtain the target surface area. These two batches were used to determine if there are any inherent differences between ball-milled and attritor-milled NiO that may affect the processing of single cells and single-cell stacks.

The material used in the evaluation described above, and new baseline batches A05211-1, E05241-1, CE05231-1, were utilized to fabricate single-cell stacks of varying cell construction. Forty-three single-cell stacks were fabricated using a 1:1:1, 2:1:1, and 1:5:1 cell construction with 1- by 1-in. and 1.6- by 1.6-in. fired dimensions.

The initial analysis of 1- by 1-in. fired stacks fabricated from A03221-1, E03221-1, and CE03231-1 showed that all three cell constructions bowed and contained cracks (visible at 70x magnification) in the cathode-electrolyte and anode corrugations and at both the anode and cathode-electrolyte corrugation/trilayer interfaces when processed. An optimum constraint weight for each cell construction was determined to eliminate bowing. However, stacks with 1:1:1 and 1:5:1 constructions consistently exhibited extensive cracking in the cathode-electrolyte and anode corrugations and corrugation/trilayer interfaces. Stacks of 1:5:1 construction had severe delaminations at the A/E interfaces, but very few cracks were observed in stacks of 2:1:1 construction. Slight hairline cracks at the cathode-electrolyte corrugation/trilayer interface were the only defects observed, as shown in Figure 4-20.

Figure 4-20. Hairline Crack at the Cathode-Electrolyte Intermediate Corrugation/Trilayer Interface (ST1374, 211)

To evaluate the effect of ball-milled NiO on the processing of single-cell stacks, 1- by 1-in. fired stacks of 1:5:1 and 2:1:1 cell construction were fabricated using Batch A02101-1. (Stacks of the 1:1:1 construction were not evaluated due to the lack of success with single cells and single-cell stacks made with that ratio.) After repeated trials, stacks with the 1:5:1 construction still contained severe delaminations at the anode/

electrolyte interface and cracks in the anode and cathode-electrolyte corrugations. However, the hairline cracks at the cathode-electrolyte/trilayer interface in the 2:1:1 stacks were dramatically reduced, particularly when the extreme edges of the cathode-electrolyte corrugations were not thoroughly bonded to the trilayer, as shown in Figure 4-21.

Figure 4-21. Incomplete Bond at the Cathode-Electrolyte Intermediate/Trilayer Interface

A modification was made in the solvent bonding of the cathode-electrolyte corrugation to the trilayer to ensure that the extreme edges of the cathode-electrolyte corrugation layer were not bonded to the trilayer. The result of this modification was quite significant. Examination of numerous 2:1:1 stacks revealed that the hairline cracks at the cathode-electrolyte/trilayer interfaces were eliminated. Presently, 1- by 1-in. fired stacks, with a cell construction of 2:1:1, can be fabricated and processed with rare observation of any defects. This modification was also implemented for the fabrication of 1:5:1 stacks, but did not seem to lessen the number of defects with this construction. Severe delamination at the anode/electrolyte interfaces was still observable.

Four single-cell stacks using a 2:1:1 cell construction and the modified solvent bonding technique with 1.6- by 1.6-in. fired dimensions were also fabricated using anode batch A02101-1 (ball milled). When processed, the first two 2:1:1 stacks exhibited severe slumping of the corrugations due to nonuniform pressing, although examination of the trilayer revealed no cracking or other defects. Observation of the remaining two unfired stacks at 70x magnification showed uniform corrugations. After these stacks were processed, no defects could be observed at the trilayers or in the corrugations. However, a slight hairline crack on a cathode/electrolyte cover layer was observed.

Four fired single-cell stacks, each 1- by 1-in. square, of the 2:1:1 and 1:5:1 cell constructions were also fabricated using baseline batches A05211-1, E05241-1, and

CE05231-1. Preliminary results indicate that the similar types of delaminations and cracks are still observable for stacks with the 1:5:1 construction. The stacks with the 2:1:1 construction did not possess any hairline cracks in the trilayer, however, a crack on a cathode-electrolyte cover layer was observed. Further analysis is necessary to determine an optimum constraint weight because all samples were bowed.

Evaluating the scalability of single-cell stacks involved increasing the footprint area from 1-in. by 1-in. (Size 1) to 1.6 in. by 1.6-in. (Size 2), and 2 in. by 2-in. (Size 3) fired dimensions. A number of single-cell stacks with Size 2 and Size 3 footprint areas were fabricated for scalability evaluation. Visual and optical microscopic examination of Size 2 stacks after processing showed slight bowing and the presence of certain types of common defects. Although attempts were made to minimize bowing by varying constraint weight, a minor degree of bowing was still observable. The defects observed in Size 2 stacks consisted of hairline cracks at the CE intermediate corrugation/trilayer interfaces and occasional cracks through the intermediate cover layers. Examination of single-cell stacks of the Size 3 fired dimensions showed defects similar to those observed in the Size 2 stacks. However, the cracking present in the intermediate cover layers of the Size 3 stacks was more severe. The bowing of the Size 3 stacks, on the other hand, was less than that observed in the Size 2 stacks.

Single-cell stacks with a Size 1 fired dimension were also processed to support testing and bonding efforts. Selection of stacks for testing and bonding purposes was based on the degree of defects and flatness for each stack. Each stack candidate was carefully scrutinized (at 70X magnification) for the presence of defects, particularly cracking within the electrolyte region. Only stacks without observable defects were selected. Several single stacks of this category were submitted for testing and bonding during this reporting period.

In addition to stack fabrication, an effort was conducted to incorporate header bars into the design of single-cell stacks, as shown in Figure 4-22. The header bars were to provide flat surfaces at the stack edges for sealing. Two types of header bars were evaluated: electrolyte (zirconia electrolyte) and electrodes (anode material and cathode material). Preliminary processing results of stacks with header bars indicated that the incorporation of header bars causes significant bowing and cracking (especially at the coverplates) in the stack.

A series of single-cell stacks, consisting of varied electrode cover layer thicknesses, were fabricated and processed. The objective of this effort was to evaluate cover thicknesses for stack flatness improvement. The standard single-cell stack cover layer green thickness is 13 mils. Table 4-4 shows the combinations of anode and cathode cover layer thicknesses evaluated.

IG-10296

Figure 4-22. Single-Cell Design with Incorporated Header Bars

TABLE 4-4		
SINGLE-CELL STACKS WITH VARIOUS COVER THICKNESSES		
Stack ID	Anode Thickness, mils	Cathode Thickness, mils
EB037-1	13	13
EB037-2	13	26
EB037-3	26	13
EB037-4	26	26

Visual and optical microscopic examination of the sintered samples indicated that fabricating single-cell stacks with 13-mil electrode cover layers gave the best results. All stacks that were fabricated with either a 26-mil anode or cathode cover layer possessed severe defects and delaminations. Although the cathode covers layers remained extremely flat in stacks constructed with 26-mil cathode covers, the anode layers within these stacks sintered to a concave shape, causing delamination and severe defects within the stacks.

An effort was made to reduce the magnitude and frequency of the defects (particularly the V-cracks commonly seen in CE corrugations) found in single-cell stacks. The approach taken to reduce these defects was to incorporate toughened components in single-cell stacks. Experiments were carried out to find the best combination of toughened layers and baseline layers when structural integrity and electrochemical performance were considered in single cells and single-cell stacks.

To find the best structural combination, matrices of single-cell discs (green dia = 1.25 in.) and single-cell stacks (green dimensions = 1.3 in. x 1.3 in.) were fabricated. Table 4-5 shows the matrices and the yields for each combination of cell and stack.

TABLE 4-5				
RESULTS OF CELLS AND STACKS FABRICATED WITH BASELINE AND MODIFIED COMPONENTS				
Component			Results	
A	E	CE	Single-Cell Disk (Yield)	Single-Cell Stack (Observation)
Baseline	Baseline	Baseline	8/10	Defect Type II
Baseline	Modified	Baseline	0/4	Defect Type IV
Modified	Baseline	Baseline	4/4	Warped
Modified	Modified	Baseline	4/4	Warped
Baseline	Baseline	Modified	4/4	No observable defects
Baseline	Modified	Modified	4/4	Defect Type III
Modified	Baseline	Modified	4/4	Warped
Modified	Modified	Modified	3/4	Warped, slumped
Defect Type II: Defect (hairline crack) barely identifiable at 70X and not found within electrolyte layer				
Defect Type III: Defect (hairline crack) easily identifiable at 70X and not found within electrolyte layer				
Defect Type IV: Defect (hairline crack) found in or through electrolyte layer				

From these results, it was concluded that a combination of baseline A, baseline E, and modified CE was structurally the best combination considered. Several 1.3-in. (green footprint area) single-cell stacks have been successfully processed and subsequently fabricated into multicell stacks using the second-step bonding technique.

A number of baseline single-cell stacks were also processed using the creep-sintering technique. Optical microscopic examination of baseline single-cell stacks after processing showed the presence of a few common defects. However, the degree of bowing was dramatically reduced compared to single-cell stacks processed by the

conventional sintering method. In addition, single-cell stacks constructed with baseline anode, baseline electrolyte and Al_2O_3 -toughened CE were fabricated and processed using the creep-sintering technique. Visual and optical examination of the stacks after processing showed the presence of very few defects and the absence of bowing. Several of these stacks were selected for multicell bonding and testing.

4.1.2.1.3 Multicell Stack Fabrication

During the course of this project ceramic bonding technology was developed to assemble the single-cell modules and single-cell stacks with interconnect plates and form testable multicell stacks. Bonding formulations evolved from slurries comprising cell components and glass frits to tapes formed from fuel cell components. It was found that roughening the surface of tapes in the green state enhanced bonding.

The bonding development effort proceeded with two objectives: (1) to identify bonding formulations and techniques that would give good electrochemical performance and (2) to supplement understanding of the bond process through characterization of bond formulations and bonded layers. These efforts culminated in bonded single-cell and two-cell stacks demonstrating good electrochemical performance.

To determine the mechanical integrity of second-step anode bonds under testing conditions, several anode-anode (A/A) and anode-interconnect (A/I) coupons were bonded with pure A and A/I composite tapes and then exposed to reducing environments. All bond formulations and configurations held after hydrogen reduction of the NiO to Ni metal. Therefore, it is concluded that anode-anode and anode-interconnect bonds have the ability to withstand testing environments.

Performance testing procedures require heating a stack to approximately 900°C twice (for current collector application) and then to 1000°C (for actual testing) making thermal cyclability an important criterion for bonding evaluation. Stacks of A-module-CE and A-module-I constructions were cycled three times from room temperature to 1000°C without delaminating. Destructive evaluation of stack interiors showed no detectable change within the bond layers after the thermal cycles.

Several types of single-cell stacks were constructed, differing in the layer used for cover plates and/or the bonding formulations. The purpose of this effort was to identify bond formulations for building multicell stacks and assessing the effect the different cover plates and bond formulations would have on performance. Table 4-6 summarizes the results obtained on stacks constructed for this effort.

As seen from Table 4-6, stacks with an interconnect plate substituting for an anode cover had poor CE bonds and a tendency to delaminate during application of the current collector. This indicates a weak bond and poor thermal cyclability. From these results and performance test results, no further work on the use of the interconnect as a cover plate along with the CE cover plate was pursued.

TABLE 4-6			
EFFECTS OF DIFFERENT COVER PLATES AND BOND FORMULATIONS			
Stack Construction	Anode Bond Formulation	CE Bond Formulation	Result
A-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds; tested
	A/I (75/25)	CE/I (25/75)	Poor bonding
	A/I (50/50)	CE/I (50/50)	Good bonding
A-sc mod-I	A/I (100/0)	CE/I (50/50)	Good bonds; tested
I-sc mod-CE	A/I (100/0)	CE/I (50/50)	Good bonds: CE plate delaminated during test preparation.
I-sc mod-I	A/I (100/0)	CE/I (50/50)	Poor CE/I bond; CE plate delaminated during test preparation.
	A/I (75/25)	CE/I (25/75)	Poor CE/I bond
	A/I (50/50)	CE/I (25/75)	Poor CE/I bond; CE plate delaminated during test preparation.
Note: sc mod means single-cell module			

In general, single-cell modules show slight bowing after processing. Modules containing baseline A, E, and CE tend to bow along the anode corrugation length. Bowing along the CE corrugation length is minimal. To compensate for the module bowing in bonding, combinations of thick and thin bonding tapes were used. This approach showed improved bonding contact in bonded stacks. Another attempt to circumvent module bowing was to polish the high points of the corrugations, thus removing the bowing. Polishing the corrugations resulted in increased contact when the polished module was bonded with the cover plates. Several flattened stacks were bonded to flat plates and processed. A cross section of a bonded single-cell stack (EE337-01) made by this technique is shown in Figure 4-23. In general, a significant improvement in the bond contact area was observed with this technique. However, the polishing technique caused hairline trilayer cracking when the sample was examined under a microscope at 70X. The effects of hairline cracks in electrolytes on stack performance are not known at present.

Based on the good performance of EE332-02 type stacks, several two- and three-cell stacks were fabricated. A set of two- and three-cell stacks were made to compare the effect of single and multiple interconnect layers and bonds against single-cell stacks. Table 4-7 lists the contents of this set of stacks. Figure 4-24 shows the polished cross section of a two-cell stack EE344-01, a sister stack to EE344-03.

F-65882

Figure 4-23. Polished Cross Section of a Single-Cell Stack Made by Bonding Polished Module with Flat Cover Plates (EE 337-01)

TABLE 4-7				
CONTENTS OF TWO- AND THREE-CELL STACKS				
Stack No.	No. of Cells	A/A Bond Formulation	A/I Bond Formulation	CE/I and CE/CE Bond Formulations
EE344-03	2	A/I(100/0)	A/I(50/50)	CE/I(50/50)
EE344-02	3	A/I(100/0)	A/I(50/50)	CE/I(50/50)
EE355-04	2	A/I(100/0)	A/I(100/0)	CE/I(50/50)
EE346-01	3	A/I(100/0)	A/I(100/0)	CE/I(50/50)

One of the two-cell stacks, EE344-03, was tested. It performed as well as a single-cell stack. The other two-cell stack, EE355-04, had better contact at the anode-interconnect interface based on the sister stack examination. The pure anode bond material appears to be better than an A/I formulation for anode corrugation-interconnect plate bonds. Testing of EE355-04 verifies the conclusion drawn from examining sister stacks. Microscopic inspection of the three-cell stack outer edges and cross sections showed a bond quality and character similar to the two-cell stacks.

Bond formulations were characterized by diametrical shrinkage, density, thermal contraction coefficient, and thermal expansion coefficient measurements. Figure 4-25 shows diametrical shrinkage and density values for the five bonding formulations used so far. Measurements were made after processing at 1250°C for 1 hr and 1350°C for 0.5 hr. The lower temperature was used for second-step bonding. Figure 4-25 shows that both shrinkage and density decreased as the interconnect was added to the anode. Conversely, for the CE-interconnect composite tapes, shrinkage and density increased with the interconnect additions. Table 4-8 lists the thermal contraction and expansion data for the bonding formulations.

Thermal contraction measurements were taken upon cooling after processing the tapes at 1250°C for 1 hr, as used for second-step bonding. Expansion was measured upon reheating to approximately 1100°C. There are minor differences in contraction and expansion between the formulations.

4.1.2.2 Cosintered Multicell Stack Fabrication

In the early stages of the project stacks were primarily formed by bonding single-cell modules and single-cell stacks to interconnect plates. However, two two-cell stacks with 0.75-in. by 0.75-in. plane were fabricated by the cosintering method and defects were analyzed. The interconnect layer of the two stacks was HUA calcium, cobalt-doped lanthanum chromite. The stacks (ST1270 and ST1271) were examined by low-energy dispersive x-ray analysis, and it was found that ST1270 contained an internal crack and ST1271 appeared to be crack-free.

Figure 4-24. Polished Cross Section of Bonded Two-Cell Stack (EE344-01)

ANODE-INTERCONNECT COMPOSITES

INTERMEDIATE-INTERCONNECT COMPOSITES

Figure 4-25. Firing Shrinkage and Density of Bonding Formulations

TABLE 4-8		
THERMAL CONTRACTION AND EXPANSION COEFFICIENTS FOR BONDING FORMULATIONS		
Formulation	Contraction, $\times 10^{-6}/^{\circ}\text{C}$	Expansion, $\times 10^{-6}/^{\circ}\text{C}$
A/I (100/0)	12.6	13.2
A/I (75/25)	13.4	13.8
A/I (50/50)	13.5	14.2
CE/I (50/50)	12.5	13.1
CE/I (25/75)	12.4	13.1
Note: Range for thermal contraction coefficient: 1086°C to 100°C. Range for thermal expansion coefficient: 100°C to 1082°C. Measurement error approximately 3.5 percent.		

Figure 4-26 shows micrographs of the (a) anode-interconnect and (b) intermediate-interconnect interfaces of ST1270. The interconnect appears to be inadequately densified and reaction layers do appear between the flat interconnect and the corrugated electrodes.

EDAX linescans were performed across the electrode-interconnect interfaces shown in Figure 4-26 at 20 equidistant locations. The results were plotted and are shown in Figures 4-27 and 4-28, along with a micrograph showing the path of the linescan. The crosshair is at the final scanned point. For the anode-interconnect interface, the EDAX suggests a high Ni content as expected in the 80- to 120-micron region of Figure 4-27a. This corresponds to the porous region in the anode between the dense regions (referring to Figures 4-26a and 4-27b) located at the anode-interconnect interface and approximately 10 microns up into the anode corrugation.

The linescan shows that the Ca has heavily migrated into the anode corrugation layer. The location of most of the Ca is between 80 and 130 microns across the sample of Figure 4-27a, corresponding to the dense reaction-zone layers within the anode corrugation shown in Figures 4-26a and 4-27b. Comparing the linescan plot of Figure 4-28a with the micrograph of the path in Figure 4-28b and also Figure 4-26b, it can be seen that the Ca level is also concentrated in the dense region along the cathode-interconnect interface. These reaction zones may be undesirable as they can introduce nonconductive phases that possess prohibitive interfacial resistances. From the analysis of ST1270, it is clear that a better interconnect material needs to be developed for cosintered multicell stacks.

(a)

(b)

F-63034

Figure 4-26. Micrographs of a Typical (a) Anode-Interconnect and (b) Intermediate-Interconnect Interface from ST1270 (Both at 160X)

(a)

(b)

F-63036

Figure 4-27. (a) Plotted Edax Linescan Results Across Anode-Interconnect Interface. (b) Micrograph Showing Trace of Linescan Path (Vertical Line Through Flat and Corrugated Layers) with Crosshairs at Linescan Endpoint

(a)

(b)

F-63037

Figure 4-28. (a) Plotted Edax Linescan Results Across Cathode-Interconnect Interface. (b) Micrograph Showing Trace of Linescan Path (Vertical Line Through Flat and Corrugated Layers) with Crosshairs at Linescan Endpoint

4.1.2.3 Plate and Bar Construction For Multicell Stacks

To meet the project goal of a 100-w stack it was decided that a 4-in. footprint cell would be desirable because it would reduce the total number of cells in the stack, making the stack easier to build. Unfortunately, the yield for 4-in. footprint single-cell modules was very low, and an alternative approach was needed. Since 4-in. footprint thin-film electrolyte cells can be made routinely, an approach using electrode bars, cells, and interconnect plates was utilized (see Figure 4-29). Based on analysis of component stresses interconnect bars were chosen to span the space between the cathode side of the single cell and the interconnect instead of cathode bars.

Baseline interconnect, anode, and cathode-electrolyte intermediate batches were used to fabricate bars measuring approximately 0.1 in. wide x 4 in. long x 0.050 in. thick. Optical microscopic examination showed some cracking in the interior of the bars. Efforts to fabricate anode and cathode-electrolyte intermediate bars wider than 0.1 in. from these batches were unsuccessful. Anode and cathode-electrolyte intermediate bars were then made using batches with a higher solids loading (A01263-1 and CE01263-1). Bars up to 0.3 in. wide and over 5 in. long were successfully fabricated from these batches. All sintered bars showed a high degree of flatness.

Preliminary experiments were conducted on two cell stacking concepts. One concept uses green bars of electrode material between the cell and the interconnect layer to form gas channels, while the other uses sintered bars of either electrode or interconnect bars. The bars were made from thick (0.035- to 0.060-in.) tapes. The experiments showed the feasibility of both concepts.

From the preliminary experiment results, two matrices of experiments were designed and conducted to assess the effect of stack bonding parameters. One matrix tested green bar bonding methods, while the other tested sintered bar stack building. Each experiment in the matrixes involved bonding of both sides of a thin-electrolyte single-cell plate to interconnect plates. Bond bars were either green or sintered (at 1400°C, 1 hr). Eighteen samples were processed, visually examined, mounted in epoxy, and cross-sectioned. All samples held together upon removal from the furnaces. An interconnect/anode bond from a green bar experiment was weakly bonded, and delaminated during visual inspection. Experimental responses were evaluated, based on the degree of bonding for each sample. For each matrix, there was one experiment with the highest response. A stack (EE492-01) (consisting of a thin-electrolyte single cell, 2x2 in., bonded to interconnect plates on both sides) was constructed and processed using parameters from the highest response experiment with sintered bars. Examination of the stack cross-sections showed excellent bonding between the electrodes of the cell and the interconnects. Figure 4-30 gives an example of the stack anode and cathode bonds. The bonds are well-formed and showed good contact between the bonding surfaces.

Due to inconsistencies in the bonding results with the ceramic bonds, a silver/palladium alloy was chosen as the bonding agent. Virtually all the tested stacks employed this technology. This alloy is used in the capacitor industry for similar purposes.

Figure 4-29. Plate and Bar MSOFC Fabrication Approach

M-01075

A. Bonding Between Thin-electrolyte Cell and Interconnect Plates (Photograph Taken at 20X)

B. Bonding Between Cell and Interconnect on Anode Side (Photograph Taken at 40X)

C. Bonding Between Cell and Interconnect on Cathode Side (Photograph Taken at 40X)

Figure 4-30. Cross Sections of Bonded Sample EE492-01

F-66133

The majority of the stacks of this construction fabricated for testing consisted of three single cells and five interconnect plates, with anode and interconnect bars. The interconnect plates and bars were fabricated from calcium-, cobalt-doped lanthanum chromite materials sintered at 1400°C in air. Anode bars were cut from green tape and fired at 1300°C. The stacks were assembled using a thin layer of silver-palladium paste on all bar-to-plate interfaces. The stack was heated in the retort furnace under argon to metallize the silver/palladium alloy.

With such a construction it was found that the stacks could be repeatedly thermally cycled in air to temperatures exceeding 1000°C with no apparent adverse effects. This was apparently due to the excellent thermal expansion matching of the anode and interconnect, the principal materials of stack construction.

A three-cell stack is shown in Figures 4-31 and 4-32.

Figure 4-31. Photograph of Three-Cell Stack After Firing

4.2 PROCESS PARAMETER STUDIES

4.2.1 Objective

The objective of the process parametric study is to identify critical fabrication parameters and to optimize the identified parameters for reliable fabrication of MSOFC cells and stacks.

F-66382

F-67564

Figure 4-32. Photograph of Three-Cell Stack with Pt Current Collectors

4.2.2 Selection of Fabrication Parameters

To optimize the process for fabricating MSOFC cells and stacks, identification of the most important variables in the process is essential. The approach for determining the parameters includes reviewing the material requirements, fabrication procedures, and processing conditions and then identifying the most important parameters. These parameters are divided into three categories: material characteristics, forming parameters, and firing conditions and techniques. Designed experiments will be conducted to investigate and optimize the effect of these variables on MSOFC fabrication.

The fabrication process for the MSOFC was critically reviewed and a list of fabrication parameters was compiled. From this compilation, the parameters considered as the most important in the MSOFC fabrication process were selected. The selected parameters of this study are listed in Table 4-9.

TABLE 4-9		
LIST OF PARAMETERS FOR PARAMETRIC STUDY		
Material Characteristics	Forming Parameters	Firing Conditions and Techniques
Particle size/surface area Particle size distribution	Mixing Mixing temperature Mixing time Method of mixing Rolling Rolling schedule Rolling temperature Rolling speed Corrugating Tape thickness Corrugating temperature Corrugating procedure Stacking Bonding medium	Heating rate Cooling rate Hold times Constraints Furnace atmosphere

4.2.3 Forming Parameters

As described in the January-March 1990 quarterly report, the parameters for the tape calendering process were selected for the parametric study, and experiments were initiated for the mixing step in the fabrication process. For the initial experiments, yttria fully stabilized zirconia was selected as the material for study.

For each of the studies performed within the process parametric study, the Taguchi method of experimental design was utilized to determine the minimum number of experiments necessary to derive the most information regarding the study. This method involves selecting the appropriate variables for a particular process and assigning each level of that variable a number. These numbers are fit into a predetermined matrix, the outcome being a set of experiments that will lead to the determination of the optimum conditions for the process.

4.2.3.1 Mixing Parameters

For the determination of the parameters that most affect the mixing step of tape fabrication, three variables were selected: mixing time, mixing temperature, and the method of mixing the binder and ceramic powder in the torque rheometer or high-temperature mixing chamber. Using the Taguchi method, a matrix of eight experiments was evaluated. The conditions of these experiments are listed in Table 4-10.

TABLE 4-10				
TAGUCHI DESIGNED EXPERIMENTS FOR MIXING PARAMETERS				
ID Number		Mixing Temperature, °C	Mixing Time, min	Mixing Method
1	TN 1293	70	10	Together
2	TN 1294	120	10	Separate
3	TN 1292	70	15	Separate
4	TN 1283	120	15	Together
5	TN 1291	70	20	Separate
6	TN 1275	120	20	Together
7	TN 1282	70	15	Together
8	TN 1269	120	15	Separate

In order to control the number of experiments required for Taguchi, only the most important variables are chosen, and the number of levels for each variable must be minimized. As a result, two to three levels of each variable were selected. First, two mixing temperatures, 70° and 120°C, were chosen because they are the extreme conditions. It is important to mix the batch at a temperature above the glass transition temperature of the binder system in order to allow the material to soften and promote complete and homogeneous mixing. The degree to which the mixing temperature is raised above this glass transition to get the best mixing is the important variable. Next, three mixing times were used in the study: 10, 15, and 20 min. The degree of mixing is highly dependent on the amount of time that the batch is subjected to high-temperature shear mixing. Too little time would result in incomplete mixing and reduced binder action; on the other hand, mixing for too long may result in degradation of the binder, especially at higher temperatures. Finally, the way in which the binder and ceramic material are added to the mixing chamber could have an effect on the homogeneity of the batch. Two methods were selected: mixing all the components together first and putting the entire mixture into the rheometer at the same time; and mixing the components of the binder system together first, putting the mixture into the rheometer to soften, and then adding the ceramic material after approximately 3 min.

Two criteria were used to determine the best combination of mixing parameters: biaxial flexure strength and bulk density. Both of these are important material properties of zirconia that would be affected by the degree of homogeneity within the tape batch. By using the values for both of these properties (resulting from the experiments outlined in Table 4-10), it was possible to determine the best set of mixing conditions. Figures 4-33 and 4-34 illustrate the change in strength and bulk density, respectively, as a function of the tape mixing conditions. The biaxial flexure strength data for the YSZ samples used in this study are shown in Table 4-11. Also included are the Weibull moduli and corresponding four-point bend strengths of the materials.

TABLE 4-11				
STRENGTH DATA FOR MIXING PARAMETRIC STUDY BATCHES				
Batch	Biaxial Strength, ksi	Weibull Modulus	Four-Point Conversion	
			Volume, ksi	Surface, ksi
1	52.0	6.7	21.9	26.3
2	47.2	8.1	23.0	30.3
3	51.3	5.0	16.1	23.0
4	46.1	6.4	18.6	25.4
5	49.1	9.2	26.1	33.6
6	43.0	4.3	11.1	16.4
7	46.3	6.3	18.4	25.2
8	34.2	4.0	8.0	12.0

Using a computer program which analyzes the data obtained for the Taguchi design, the optimized mixing conditions have been determined. The best properties result from the batch mixed together at 70°C for 10 min. This result also corresponds to the data in Figures 4-33 and 4-34, as well as Table 4-11.

4.2.3.2 Rolling Parameters

To determine the best method to roll the tape batches, a more extensive set of experiments had to be investigated. In this case, the variables chosen were the rolling schedule, the difference in speed between the two rolls, and the tape storage time before thermal processing. Additional levels for the schedule and storage time made it necessary to expand the Taguchi matrix to 16 experiments. Table 4-12 contains a list of the experiments in the designed plan.

The rolling schedule is the first variable which may affect the overall properties of the tape. Depending on how fast the distance between the two rolls is decreased and how many passes each piece of tape experiences per setting, the characteristics of the

Figure 4-33. Bulk Density Versus Composition for the Mixing Parametric Study Electrolyte Batches

Figure 4-34. Biaxial Flexure Strength Versus Composition for the Mixing Parametric Study Electrolyte Batches

TABLE 4-12

TAGUCHI DESIGNED EXPERIMENTS FOR ROLLING PARAMETERS

Batch	Rolling Schedule	Rolling Speed, ft/min	Storage Time
1	Original ¹	35/34	24 hr
2	Original	35/34	1 wk
3	Slow ²	35/34	24 hr
4	Slow	35/34	1 wk
5	Fast ³	35/34	24 hr
6	Fast	35/34	48 hr
7	Very fast ⁴	35/34	24 hr
8	Very fast	35/34	48 hr
9	Original	40/34	24 hr
10	Original	40/34	48 hr
11	Slow	40/34	24 hr
12	Slow	40/34	48 hr
13	Fast	40/34	24 hr
14	Fast	40/34	1 wk
15	Very fast	40/34	24 hr
16	Very fast	40/34	1 wk

¹Change the distance between the rolls by 10 mils/five passes each.

²Change the distance between the rolls by 5 mils/five passes each.

³Change the distance between the rolls by 25 mils/five passes each.

⁴125/50/10 mils/five passes each.

tape may change. Another variable is the difference in speed between the two rolls, which will affect both the texture, surface finish, and homogeneity of the resulting tape. Finally, the amount of time that the tape has to relax before thermal processing may affect certain properties of the material, for example springback and shrinkage.

At this time only one criterion has been used to analyze the results of the parametric study experiments: biaxial flexure strength. Additional criteria, such as bulk density, a fired property, and tape tear strength, a prefired property, may be investigated in the near future.

Preliminary results from the rolling parametric study with consideration to the strength of the material are shown in Table 4-13. The Taguchi analysis has shown that the optimum rolling conditions are rolling at the slow schedule, with the rolls set at 40/34 ft/min, and then allowing the tape to sit for at least 1 week before firing. These conditions may change when other criteria are considered.

TABLE 4-13				
STRENGTH DATA FOR ROLLING PARAMETRIC STUDY BATCHES				
Batch	Biaxial Strength, ksi	Weibull Modulus	Four-Point Conversion	
			Volume, ksi	Surface, ksi
1	39.2	4.1	9.5	14.1
2	45.4	8.4	22.7	29.7
3	45.5	7.5	21.0	27.9
4	40.6	2.7	4.7	7.7
5	38.4	5.6	13.6	19.1
6	40.6	2.3	3.3	5.5
7	42.6	6.3	16.9	23.2
8	44.4	2.5	4.4	7.2
9	42.9	7.3	19.4	25.9
10	44.5	3.5	8.5	13.0
11	41.8	7.8	19.9	26.2
12	42.3	6.0	16.1	22.2
13	44.1	4.1	10.7	15.9
14	38.9	3.8	8.4	12.7
15	39.8	4.3	10.3	15.2
16	38.8	3.7	8.1	12.3

4.2.3.3 Thermal Processing Parameters

The thermal treatment of the MSOFC stacks is an integral part of the overall processing of the fuel cell. It is during this time that the appearance of cracks from binder removal or sintering may occur. In addition, any problems with the differences in thermal expansion among the materials will play a major role. It is important to understand why each segment of the thermal process is necessary to tailor the outcome of the firing schedule.

The Taguchi method of experimental design was used to determine the experiments necessary to investigate the effect of the thermal processing parameters. In this case, there were quite a few possible parameters from which to choose, making the experimental matrix extremely large. As a result, only the most important ones were selected.

Figure 4-35 illustrates the relationship among the seven parameters selected for this investigation: the actual furnace being used, the position of the samples in the furnace, the method of sample constraint, the initial heating rate, the second heating rate, the high temperature hold time, and the final cooling rate. This figure shows the interactions between certain variables (indicated by tie lines) that can be ascertained from the experimental results. The importance of these parameters is discussed in the following paragraphs.

IG-06418

Figure 4-35. Taguchi Experimental Design Matrix for Firing Parametric Study

The first three variables are associated with the placement of the samples during the firing process. In the course of the experimental work done at ASE, there are several different furnaces that may be utilized. By incorporating the actual furnace used for the thermal treatment into the parametric study, it may be determined if more consideration should be placed on maintaining the use of a particular furnace for consistent results. In addition, the position of the samples within the furnace may play an important role. Thermal gradients within a furnace can cause samples near the bottom of the furnace to sinter differently from those near the top. Finally, it is important to maintain flatness during firing, so constraints are applied. This constraint has varied from the application of direct pressure to the samples (in the form of an additional setter plate on top) to the use of shims to support a setter plate over the samples. These shims, about 3 to 5 mils higher than the original thickness of the sample, would force the material to stay relatively flat without applying direct pressure.

The other four variables in the analysis are related to the temperature profile used in the sintering process. By adjusting the initial heating rate, it may be possible to speed up the first part of the firing schedule, which would help in cutting down on production time in the future. On the other hand, if the second heating rate is decreased from that which is presently used, allowing the samples more time to go through binder removal, it may help to relieve more of the stresses that build up during that part of the process. Next, the high temperature hold may be adjusted to allow for better densification during sintering. On the other hand, if a shorter time period is adequate, it would allow for the shortening of the schedule. Finally, the cooling rate may affect the final properties of the stack because cracks may form upon cooling. Decreasing the cooling rate may accommodate stresses resulting from differences in thermal expansion between layers.

The experiments that resulted from the Taguchi analysis are listed in Table 4-14. The criteria for evaluating the results are the same as those used for the two previous studies—biaxial flexure strength and microstructural characterization.

TABLE 4-14							
TAGUCHI-DESIGNED EXPERIMENTS FOR FIRING PARAMETERS							
Batch	Furnace No.	Constraint	Position	Initial Heating Rate, °C/hr	Second Heating Rate, °C/hr	High Temperature, Hold, hr	Cooling Rate, °C/hr
1	3	D	L	16.8	11.1	0.5	50
2	3	D	H	30.0	11.1	1.0	100
3	3	D	H	16.8	18.0	1.0	50
4	3	D	L	30.0	18.0	0.5	100
5	3	S	L	30.0	11.1	1.0	50
6	3	S	H	16.8	11.1	0.5	100
7	3	S	H	30.0	18.0	0.5	50
8	3	S	L	16.8	18.0	1.0	100
9	4	D	L	16.8	11.1	1.0	50
10	4	D	H	30.0	11.1	0.5	100
11	4	D	H	16.8	18.0	0.5	50
12	4	D	L	30.0	18.0	1.0	100
13	4	S	L	30.0	11.1	0.5	50
14	4	S	H	16.8	11.1	1.0	100
15	4	S	H	30.0	18.0	1.0	50
16	4	S	L	16.8	18.0	0.5	100

4.3 DEFECT ANALYSIS

4.3.1 Objective

The objective of this task is to analyze defects in MSOFC cells and stacks and to correlate identified defects to material and fabrication parameters. Correlation can be used to suggest fabrication modifications to minimize defects.

4.3.2 Status-Literature Survey and Defect Classification

A literature survey was made to obtain information on defects in ceramics, defect classifications, and nondestructive evaluation of materials.

A tentative defect classification system was developed which illustrates ten defects commonly observed in MSOFC stacks. The classification system was developed by observing defects occurring in MSOFC stacks fabricated to date. The classification system, illustrated in Table 4-15, is tentative and the defect classification number does not indicate the severity of the degree of occurrence of the defect.

TABLE 4-15	
DEFECTS IN MSOFC'S	
Defect or Flaw	Abbreviation/Classification
No defect	0
Edge deformation	1
Warping	2
Corrugation slumping	3
Incomplete bonding	4
Delamination	5
Setter plate damage	6
Crack-parallel to anode or cathode-expansion	7
Crack-parallel to anode or cathode-contraction	8
Transverse crack	9
Internal crack	10
Failure	11

Examples of some of the defects observed in MSOFC stacks and modules are shown in Figures 4-36 and 4-37. Figure 4-36(a) is an exaggerated example of warping that has been observed in MSOFC stacks. An illustration of corrugation slumping is shown in Figure 4-36(b). This flaw results when the anode or cathode corrugated layer collapses onto itself during binder burnout. Damage due to the stacks adhering to the

(a)

(b)

(c)

Figure 4-36. Defects in MSOFC's

F-59637

(a)

(b)

(c)

(d)

Figure 4-37. Other Types of Defects in MSOFC's

setter plates is shown in Figure 4-36(c). As shown in Figure 4-36(c), adhesion of the stack or frictional forces on the stack during shrinkage result in small tears and abrasions on the surface of the stack.

Examples of the more severe flaws observed are illustrated in Figure 4-37(a) through 4-37(d). Figures 4-37(a) and 4-37(b) show typical examples of surface cracks observed in the MSOFC stacks. Figure 4-37(c) and 4-37(d), however show more severe cracking problems, such as internal cracks and cracks that traverse the entire sample.

A frequency distribution of the defects from some of the early stacks, listed by classification, is shown in Figure 4-38. This figure shows that the majority of the defects are related to cracking (classification numbers 7 through 11) of the MSOFC stacks. To further analyze this problem, several experiments were designed to evaluate the effect of thermal expansion mismatch between layers on the cracking behavior. In these experiments, the anode composition was modified to create a series of compositions with a range of thermal expansion coefficients. The fabricated tapes were evaluated during binder burnout and sintering as individual single layer tapes and in trilayer configurations. The tapes were further evaluated for thermal expansion characteristics and for defects that form as a result of the different thermal expansion coefficients.

Figure 4-38. Frequency of Defects Occurring in Stacks
(Refer to Table 4-15 for List of Defects)

B-21740

A study was undertaken to determine the effects of thermal expansion and contraction on defect formation. For this task, five anode batches were fabricated in

which the Ni content varied from 25 volume-percent to 55 volume-percent. Small disks of the various anode tapes, 1.25-in. in dia, were sintered at 1350.5°C for 1 hr, and the diametrical shrinkage was measured. The shrinkage measurements, given in Table 4-16, essentially show the increase in shrinkage with increasing Ni content in the tape.

TABLE 4-16	
PERCENT DIAMETRICAL SHRINKAGE AS A FUNCTION OF NI CONTENT IN ANODE	
Ni Content, Volume-Percent	Shrinkage, Percent
25	18.0
35	18.4
40	18.6
45	18.7
55	18.7

The anode tapes were used to form trilayer tapes with electrolyte and cathode layers. The electrolyte and intermediate tapes were the same; only the anode changed in this study. Trilayer tapes, 2 in. by 2 in., were sintered at 1350.5°C for 1 hr. All the trilayers, with the exception of the one with the anode containing 25 volume-percent Ni, cracked. The trilayer with the anode containing the highest concentration of Ni (55 volume-percent) delaminated from the electrolyte. The number of cracks observed decreased with decreasing Ni content in the anode.

Forty-three single-cell stacks were fabricated and defects were analyzed. The stacks had anode:electrolyte:cathode-electrolyte intermediate (A/E/CE) thickness ratios of 1:1:1, 1:5:1, and 2:1:1, and footprint area dimensions of 1 by 1 in. or 1.6 by 1.6 in. Initially, stacks of all three thickness ratios, with cell dimensions of 1 by 1 in., were sintered and evaluated. All the cells were slightly warped. Warping was eliminated in subsequent evaluations by adjusting constraint weight for each cell. Stacks with a 1:1:1 or 1:5:1 A:E:CE trilayer cracked extensively across the trilayers and the corrugations. In addition, stacks with a 1:5:1 configuration delaminated at the A:E interface.

Stacks with a 2:1:1 configuration had only minor cracks at the interface between the CE corrugations and the trilayer. It was observed that the outer edges of the CE corrugations were not bonded to the A/E/CE trilayer. A modification was made in the bonding process to ensure complete bonding of the corrugates to the trilayer. After iterative development of the fabrication and processing parameters, examination of the 2:1:1 stacks revealed that the cracks at the corrugation-trilayer interface were eliminated. At present, stacks with a 2:1:1 thickness ratio can be fabricated without any observed defects.

A simplified defect classification system was developed to evaluate sintered single-cell modules. This classification is possible because of the to frequent occurrence of certain defects in sintered modules. The classification system is based on visible observation and optical microscopic inspection along the sides of the module at 70X magnification. A higher category value indicates that the defect is more severe in terms of its effect on module structural and electrochemical performance. Sintered modules are classified by their highest value defect observed. The simplified system is shown in Table 4-17.

TABLE 4-17	
SIMPLIFIED DEFECT CATEGORIES FOR SINGLE CELL MODULES	
Category	Description
I	No defect found
II	Defect (hairline crack) barely identifiable at 70X and not found within electrolyte layer
III	Defect (hairline crack) easily identifiable at 70X and not found within electrolyte layer
IV	Defect (hairline crack) found in or through electrolyte layer
V	Macroscopic crack or fracture

Defect examination of one hundred 1-in. modules showed the following distribution:

<u>Defect Type</u>	<u>Number of Modules</u>
Type I	57
Type II	7
Type III	17
Type IV	8
Type V	11
Total	100

Flatness characterization was performed on modules containing different CE baseline batches. Optical comparator measurement results, summarized in Table 4-18 (made on 1-in. footprint single-cell modules using either CE08291-1 or CE03122-1 baseline CE layers), revealed no difference in sample flatness. Samples with these gaps have been used in multicell stack bonding.

TABLE 4-18		
COMPARATOR MEASUREMENTS ON SINGLE-CELL MODULES USING DIFFERENT CE LAYERS		
CE Layer Contained	Average Gap, in.	Standard Deviation, in.
CE08291-1	0.0037	0.0026
CE03122-1	0.0032	0.0023

4.4 MATERIALS AND PROCESS SPECIFICATIONS

4.4.1 Objective

The objective of this task is to develop baseline material and process specifications for the fabrication of the MSOFC. The specifications will document the characteristics of starting materials and process parameters and identify acceptable ranges for each variable.

4.4.2 Specification Development

MSOFC fabrication flow charts were reviewed to identify all the material and process specifications that must be created. A list of specifications was developed for the MSOFC based on the current fabrication process. This specification list consisted of 9 material specifications and 20 process specifications. A format for the material specifications has been developed; these documents contain all the pertinent purchasing and receiving inspection requirements and are designed to permit integration into the ASE material and process specification electronic data base. The format is illustrated in Figure 4-39 and its major characteristics are as follows:

- (a) The areas marked 1 contain identifiers which permit integration into the existing ASE material and process specification data base.
- (b) The area marked 2 contains a brief general description of the material to be purchased.
- (c) The area marked 3 identifies the manufacturer of the material and its commercial and Government entity (CAGE) code if it is presently supplying materials to the Government or Government suppliers.
- (d) The area marked 4 identifies the manufacturer's product number and name.
- (e) The area marked 5 contains information on package size.
- (f) The area marked 6 contains information on package size.
- (g) The area marked 7 contains shelf life and storage requirements.
- (h) The areas marked 8 reference other pertinent material or process specifications.

AiResearch Los Angeles Division		CAGE CODE 70210	MATERIAL PROCUREMENT STANDARD		DOCUMENT NO. MPS	1	REV LTR
MATERIALS ENGINEERING					ISSUE DATE	REV DATE	PAGE 1 OF
CATEGORY INDEX 1	CATEGORY TITLE 1		PACKAGE SIZE IDENTIFICATION 5				
		MATERIAL DESCRIPTION 2		NOTE TO SUPPLIER: IDENTIFY PACKAGES AND SHIPPERS WITH DOCUMENT AND SIZE IDENTIFICATION NUMBER			
MANUFACTURERS PRODUCT IDENTIFICATION NUMBER (S) 4	MANUFACTURER (S) AND CAGE (S) 3		OTHER DESIGNATIONS (REF) 6				
MANUFACTURERS PRODUCT NAME (S) 4			COMPUTER-PREPARED DOCUMENT. CHANGES MUST BE INCORPORATED VIA THE COMPUTER SYSTEM.				
SHELF LIFE AND STORAGE CONDITIONS 7			APPLICABLE MATERIAL SPECS 8				
TYPICAL USES 9			APPLICABLE PROCESS SPECS 8				
TYPICAL PROPERTIES AND HAZARD DATA 11			QUALITY ASSURANCE PROVISIONS 10				
			UNLESS SPECIFIED OTHERWISE, INSPECT FOR CORRECT MATERIAL IDENTITY, LABELING, AND SHELF LIFE INFORMATION. ACCEPTANCE STAMP EACH MATERIAL CONTAINER UNLESS BULK SHIPMENT PROHIBITS.				
EDITED BY		DATE	PROJECT		DATE	OTHER	
PREPARED BY		DATE	MATLS ENGRG		DATE	CONFIG MANAGEMENT	

Figure 4-39. Preliminary Material Specification Format

AiResearch Los Angeles Division	CAGE CODE 70210	MATERIAL PROCUREMENT STANDARD	DOCUMENT NO MPS		REVLTR
MATERIALS ENGINEERING			ISSUE DATE	REV DATE	PAGE 2 OF
<div style="border: 1px solid black; border-radius: 50%; width: 40px; height: 40px; display: flex; align-items: center; justify-content: center; margin: 0 auto;">12</div>					

Figure 4-39. (Continued)

- (i) The area marked 9 contains a brief description of the manner in which the material will be used.
- (j) The area marked 10 contains receiving inspection requirements.
- (k) The area marked 11 contains the material property requirements and material hazard data derived from the Material Safety Data Sheet or other manufacturer-supplied information.
- (l) The area marked 12 (on the second and all subsequent pages) provides supplemental space to complete any information that could not be placed on the first page.

A format for the process specifications was developed. These documents contain requirements and procedures for fabricating the MSOFC. The process specifications contain the following sections:

- (a) Scope: This section describes the purpose and technical coverage of the specification. It also defines any special classification of parts (type, grade, composition), describes any limitations on the process, and establishes how the document is authorized within the ASE engineering documentation system.
- (b) Applicable Documents: This section contains a list of all pertinent documents referenced in the specification along with their title and source.
- (c) Materials and Equipment: This section lists all materials and equipment needed to perform the operations described. The list of materials will contain a source or a specification to which the material must conform. Also, the instructions for preparing any required material compositions are presented here. The list of equipment contains a brief description of the equipment, any special requirements that it must meet, and a source for obtaining it.
- (d) Procedure: This section contains a description of the procedures to be followed to accomplish the task described in the scope.
- (e) Quality Assurance: This section contains a description of the requirements that the process, equipment, or product must meet and all examinations and tests needed to confirm that those requirements have been met. Lot inspection, process control, operator certification, equipment certification and maintenance, and record keeping requirements are among the topics addressed in this section.
- (f) Notes: This section contains safety requirements and any general information that pertains to the process being performed. It may contain definitions, related documents, or any other supplementary information that aids in the performance of the process.

A complete listing of the final MSOFC materials and process specifications is presented in Table 4-19.

4.5 MATERIALS SUPPLIER IDENTIFICATION

Potential raw material suppliers were identified through several means, including literature surveys, contact with present suppliers, and recommendations from contacts in the industry. Multiple suppliers were sought for most of the materials except for commercially available commodity material. Well documented quality commodity materials are known to be readily available in large quantities from several suppliers, and therefore only the supplier who is currently used was contacted.

The suppliers contacted are listed in Table 4-20 by the specific materials for which they were considered.

4.5.1 Objective

The primary objective of this subtask is to identify potential raw material suppliers that are capable of (1) producing materials that consistently meet the requirements of chemistry, particle size, and surface area, and (2) supplying all or a substantial portion of the annual usage requirements. Potential suppliers for each of the MSOFC materials will be identified. At present, several of the key materials are supplied by Japanese sources, research laboratories, or universities. The availability of these materials, domestically, in commercial quantities, and at reasonable cost must be addressed.

4.5.2 Approach

The approach used for this subtask was to directly contact potential material suppliers to discuss material specifications and requirements, obtain the necessary information for evaluating those vendors, and recommend the most compliant suppliers. This effort involved several steps:

This effort involved several steps:

- (a) Specification generation—A detailed set of specifications was prepared for each type of material. Requirements for particle size distribution, surface area, purity, density, and other pertinent properties were established.
- (b) Supplier identification—Suppliers who potentially could provide one or more of the required materials were identified following a literature review and direct vendor contact.
- (c) Potential supplier contact—Suppliers having the potential to meet both material and quantity requirements were contacted. These suppliers were presented with a detailed set of specifications for the materials as well as projected annual usage requirements with which to comply. Each vendor was asked to submit any exceptions he might have to the specifications, a price per kilogram in 1990 dollars, and an estimate of his ability to supply all or a substantial portion of the annual requirement.

TABLE 4-19	
MSOFC MATERIALS AND PROCESS SPECIFICATIONS	
Number	Title
Material Procurement Standard	
MPS700001	Ytria Stabilized Zirconium Oxide
MPS700002	Lanthanum Strontium Manganese Oxide
MPS700003	Lanthanum Chromium Strontium Oxide
MPS700004	Aluminum Oxide
MPS700005	Nickelous Oxide
MPS700006	Silicon Dioxide
MPS1200001	Plasticizer
MPS1200002	Binder
MPS1200003	Rice Starch
MPS1200004	Stearic Acid
MPSXXXXXX	Zirconia Cement
MPSXXXXXX	Platinum Ink
MPSXXXXXX	Platinum Powder
MPSXXXXXX	Platinum Screen
MPS1200006	Aerosol OT-B
MPSXXXXXX	Silicon Spray
Assembly and Fabrication	
AF546	Fuel Cell Electrolyte Fabrication
AF547	Fuel Cell Cathode Fabrication
AF548	Fuel Cell Anode Fabrication
AF549	Fuel Cell Cathode/Electrolyte Intermediate Fabrication
AF550	Particle Size Analysis
AF551	Surface Area Analysis
AF552	Fuel Cell Interconnect Fabrication
AF553	Fuel Cell Multilayer Laminate
AF556	Fuel Cell Stack Cosintering Process

TABLE 4-19	
MSOFC MATERIALS AND PROCESS SPECIFICATIONS (Continued)	
Number	Title
AF556	Fuel Cell Stack Cosintering Process
AF557	Fuel Cell Single-cell Fabrication
AF558	Fuel Cell Two-step Cofiring Process
AF559	Dilatometry Analysis
AF560	Porosimetry Analysis
AFXXX	Thin-electrolyte Single-cell Fabrication
Testing	
AF561	Fuel Cell Single-cell Performance Testing
AF562	Fuel Cell Stack Performance Testing
AF563	Fuel Cell Impedance Testing
AFXXX	Thin-electrolyte Stack Testing

- (d) Supplier reply evaluation—Each reply from a vendor was evaluated for compliance with the specifications, price, and ability to meet the annual material requirement. Items such as domestic vs foreign location and country of incorporation were also considered. Suppliers were contacted if clarification of details was necessary.
- (e) Supplier reply compilation—Results of all the vendor replies were tabulated and compiled so that a comparison between suppliers could be made.
- (f) Evaluation and recommendation—Following the completion of all vendor replies, several suppliers for each material were selected as the most compliant. These suppliers have been recommended as being the primary or secondary source for each material.

TABLE 4-20	
POTENTIAL SUPPLIERS CONTACTED	
<u>Zirconia</u>	<u>Nickelous oxide</u>
Allied-Signal	Alfa
Magnesium electron	Aldrich
Rhone-Poulenc	Cerac
TAM	J. T. Baker
TOSH	
Trans-Tech	<u>Anode Additive 1</u>
Z-Tech	
<u>Lanthanum chromite</u>	Meller Optical
	Alcoa
Allied-Signal	<u>Binder</u>
Cerac	
HUA	Union Carbide
Molycorp	
Rhone-Poulenc	<u>Plasticizer</u>
SSC	
Trans-Tech	Monsanto
<u>Lanthanum manganite</u>	<u>Anode Additive 2</u>
Allied-Signal	Cabot Corp.
Cerac	
HUA	<u>Pore Former</u>
Rhone-Poulenc	
SSC	E M Science
Trans-Tech	

4.5.3 Replies from Suppliers

Information received from potential suppliers obtained through returned questionnaires, telephone conversations, direct discussions, and company literature was tabulated and summarized. A detailed discussion of the replies would exceed the scope of this quarterly report. Therefore, a discussion of only one of the more important parameters, raw material price, is presented in the next section. A brief summary of the replies from the recommended suppliers for each raw material is presented in para. 4.5.6.

4.5.4 Price Summary

A summary of the estimated bulk prices received from the potential suppliers for each material is presented in Table 4-21. Prices varied substantially for some materials. Broad variations in price were expected for some materials (such as lanthanum

TABLE 4-21

SUPPLIER ESTIMATED BULK PRICES

Material	METC1 Cost Study Price, per kg	Supplier	New Estimated Price, per kg
Zirconia	\$9.00	Allied-Signal	\$45.00
		Magnesium Elektron	\$80.00
		Rhone-Poulenc	\$40.00 to \$50.00
		TAM	\$41.00 to \$48.00
		TOSOH	\$55.00 to \$60.00
		Trans-Tech	\$20.00 to \$50.00
		Z-Tech	\$55.00 to \$66.00
Lanthanum chromite	\$80.00	Allied-Signal	\$100.00
		Cerac	\$400.00
		HUA	\$50.00 to \$60.00
		Molycorp	\$26.00 to \$33.00*
		Rhone-Poulenc	\$100.00
		SSC	\$100.00 to \$125.00
		Trans-Tech	\$60.00 to \$5.00
Lanthanum manganite	\$80.00	Allied-Signal	\$100.00
		Cerac	\$400.00
		HUA	\$40.00 to \$50.00
		Rhone-Poulenc	\$100.00
		SSC	\$100.00 to \$125.00
		Trans-Tech	\$50.00 to \$65.00
Nickelous oxide	\$4.50	Aldrich	**
		Alfa	**
		Cerac	\$21.00
		J. T. Baker	\$26.00 to \$35.00
Anode Additive 1	\$1.50	Alcoa	\$2.00
		Meller Optics	\$2.00
Binder	\$3.50	Union Carbide	\$8.00
Plasticizer	\$3.50	Monsanto	\$2.00
Anode Additive 2	NA	Cabot Corp	\$10.00
Pore former	\$3.50	E M Science	\$20.00
* Required calcining and milling			
** Research lots only			

manganite and lanthanum chromite) due to uncertainty as to their method of manufacture, yield, economies of scale, and projected raw material costs. In several cases, the estimated prices were substantially higher than those used in the METC1 manufacturing cost study. For other materials, these prices are lower than those in the cost study. It should be noted that purity level appears to be the prime driving force of price for these materials. In some cases, a slight reduction in the required purity level can reduce the price significantly.

The impact that typical material prices obtained through this study have on total material costs compared to those of the METC1 study are presented in Table 4-22. The table presents the 1988 and economic costs for raw materials as reported by Combustion Engineering (CE) in the METC1 manufacturing cost study in comparison with the typical costs reported in this study.

The total annual material costs presented in Table 4-22 are calculated for the co-flow MSOFC design. The METC1 study reported total annual material costs of \$29.5M and \$9.6M for the 1988 and economic scenarios respectively. This study concludes that typical raw material prices obtained through an actual supplier survey yield an annual raw material cost of \$18.7M. This cost falls nearly midway between the two cost levels reported in the METC1 study. Analysis of the estimated prices for each material is presented in the following subparagraphs.

4.5.4.1 Zirconia

Prices range from \$20/kg to \$80/kg, the average price being \$52/kg. This range is well above the price of \$9/kg that was used in the METC1 manufacturing cost study. The lower prices were submitted by those companies not currently supplying the powders in commercial quantities. Present-day commercial suppliers who undoubtedly have more experience on which to predict future prices tended to submit quotations at the high end of the range.

4.5.4.2 Lanthanum Chromite

Prices for this material range from \$50/kg to \$400/kg, the average price being \$115/kg. The cost of \$80/kg used in the METC1 cost study falls within this range. The high end price of \$400/kg was for small-scale batches from a company not capable of scaling up production. The low end price of \$50/kg came from the ex-supplier of this material, who is no longer in business. A price of \$60 to \$75/kg (which is lower than the cost study price) was estimated for this material by Trans-Tech.

4.5.4.3 Lanthanum Manganite

The range of prices for this material was \$40/kg to \$400/kg with the typical price being \$100/kg. The high and low prices for this material correlate closely by supplier with the prices for lanthanum chromite. Trans-Tech estimated \$50 to \$65/kg, which is lower than the \$80/kg price used in the METC1 cost study.

TABLE 4-22

COMPARISON OF RAW MATERIALS COSTS, METC1 VS METC2

Raw Material	Weight/Year, kg	CE Manufacturing Cost		Study Estimates		Task 3.5 Identification of Material Suppliers	
		1988 Cost, per kg	Total Cost	Economic Cost	Total Cost	Survey Cost	Total Cost
Yttria-stabilized zirconia	158,600	\$13.00	\$2,061,800	\$9.00	\$1,427,400	\$50.00	\$7,930,000
Sr-doped lanthanum manganite	52,800	\$275.00	\$14,520,000	\$80.00	\$4,224,000	\$100.00	\$5,280,000
Sr-doped lanthanum chromite	45,000	\$275.00	\$12,375,000	\$80.00	\$3,600,000	\$100.00	\$4,500,000
Nickelous oxide	25,300	\$6.00	\$151,800	\$4.50	\$113,850	\$25.00	\$632,500
Anode additive #1	3,200	\$2.50	\$8,000	\$1.50	\$4,800	\$10.00	\$32,000
Poreformer	6,200	\$5.00	\$31,000	\$3.50	\$21,000	\$10.00	\$62,000
Binder	28,300	\$5.00	\$141,500	\$3.50	\$99,050	\$8.00	\$226,400
Plasticizer	28,300	\$5.00	\$141,500	\$3.50	\$99,050	\$2.00	\$56,600
Solvent	2,000	\$5.00	\$10,000	\$3.00	\$6,000	\$3.00	\$6,000
Ceramic cement	1,000	\$10.00	\$10,000	\$8.00	\$6,000	\$8.00	\$8,000
	350,700		\$29,450,600		\$9,603,500		\$18,733,500

* Material quantities are as based on the CE manufacturing cost study

4.5.4.4 Nickelous Oxide

Prices ranged from \$21/kg to \$35/kg for this material, which are much higher than the \$4.50/kg cost used in the manufacturing cost study. This material is extremely price sensitive to purity. A slight decrease in purity level would drop the price substantially.

4.5.4.5 Anode Additive 1

Prices ranged from \$2/kg to \$20/kg for this material. A price of \$1.50/kg was used in the METC1 cost study. This material accounts for a small percentage of the total material used in fabricating a fuel cell and therefore has minor impact on the total raw material cost.

4.5.4.6 Binder

The bulk price for the organic binder is \$8/kg, which is more than double the \$3.50/kg price used in the METC1 cost study. It is doubtful that this price could be reduced further since the material is already manufactured in bulk and is shipped in truckload lots.

4.5.4.7 Plasticizer

The bulk price for plasticizer is \$2/kg, which is almost half the \$3.50 price used in the METC1 cost study. The material is currently produced in bulk quantities and can be shipped in tanker truck lots.

4.5.4.8 Anode Additive 2

Bulk price for this material is currently \$10/kg. This material accounts for a small percentage of the total material used in fabricating a fuel cell and therefore has minor impact on the total raw material cost.

4.5.4.9 Pore Former

The bulk price for the grade of pore former currently used in anode and cathode formulations is \$10/kg, which is substantially higher than the \$3.50/kg price used in the METC1 manufacturing cost study. Cheaper grades of pore former that would perform adequately might be available.

4.5.5 Supplier Evaluation Criteria

Evaluation of the potential suppliers was conducted using an objective numerical rating system. The system utilized a numerical rating of each supplier's response on the six most important criteria: compliance with material property specifications, price, ability to supply the total estimated annual requirement, experience, domestic vs foreign ownership, and any other pertinent criteria. The rating system was used to compare suppliers for each type of material. A rating value ranging from 5 to 1 was awarded to each supplier for each of the six criteria. A rating of 5 represented the most desirable supplier and a rating of 1 the least desirable supplier for a specific evaluation criterion. The rating process for each of the evaluation criteria is described in the subparagraphs that follow.

Each criterion was given a weighting value corresponding to its importance in terms of the other criteria. The most critical criterion was compliance with the material property specifications, which had a weighting value of 5. Therefore, a supplier who rated a 4 for that criterion received 20 points (4 rating points times the 5 weighting factor) toward his overall evaluation. Price and ability to supply the annual requirement of material were rated next in importance, with weighting factors of 3 and 2 assigned respectively. The other criteria (experience, domestic supplier, and other) were deemed of lesser importance, and thus were given a weighting factor of 1. The highest possible point total for a supplier was 65.

4.5.5.1 Material Specification Compliance

Proven compliance with all of the requirements of chemistry, particle size, surface area, and reproducibility received a value of 5. Suppliers failing to meet one or more of these criteria were rated accordingly.

4.5.5.2 Price

The lowest price for a specific material received a 5, the most expensive received a 1, and prices in between were rated accordingly.

4.5.5.3 Supply

Proven ability to supply a material in the quantities estimated to reflect the total annual requirement received a rating of 5, which essentially was awarded only to commercial suppliers who currently produce the raw material in sufficient quantity. Suppliers who currently commercially supply raw materials that are similar to a specific material and who anticipate the ability to supply the total estimated annual requirement were given a rating of 3. Anticipated ability to supply only a portion of the annual requirement or research quantities was awarded a rating of 2 and 1, respectively.

4.5.5.4 Experience

Suppliers who currently supply an acceptable material to the program were given a rating of 5. Suppliers who have extensive experience in producing a specific type of raw material but who have no direct experience with ASE on this particular program were awarded a 3 or 4 rating. Suppliers who have little commercial experience in producing a material were given a rating of 2 or 1.

4.5.5.5 Domestic Supplier

Domestic suppliers that are U.S. owned were rated a 5. Domestic suppliers who are foreign owned were rated a 3. Foreign suppliers who are also foreign owned were rated a 1.

4.5.5.6 Other

This category provided for the awarding of points to a supplier when a special condition exists. For example, points were awarded to suppliers who currently provide materials to other developers of solid oxide fuel cells.

4.5.6 Supplier Selection

Suppliers were evaluated and ranked by criteria for each raw material. Based on a combination of both the numerical evaluation and an objective appraisal, the top two suppliers for each raw material were identified. The top-rated supplier for each material is regarded as the primary supplier; the next-highest supplier is the secondary supplier. The subparagraphs below present the primary and secondary suppliers for each material along with the basis for their selection.

4.5.6.1 Zirconia

Primary: Trans-Tech and TAM
Secondary: TOSOH

Trans-Tech and TAM were tied for primary supplier with scores of 52. Both companies have the ability to tailor the zirconia to meet specific particle size and surface area specifications. While Trans-Tech does not have the capacity to supply the entire estimated annual requirement, its capability to possibly produce nickelous oxide-coated zirconia powders to meet specifications warrants special consideration.

TOSOH is the current supplier of zirconia powder for the fuel cell programs. Despite its not being a domestic supplier and its price not being as low as that of the other suppliers, TOSOH still rated high enough to be considered the secondary supplier. Current problems with inconsistent particle size and surface areas from lot to lot would be eliminated when large volumes of material are ordered and tighter QA controls are implemented.

4.5.6.2 Lanthanum Chromite

Primary: Trans-Tech
Secondary: SSC

Trans-Tech was the highest scorer for this material and thus was awarded its primary supplier status. Recent evaluations of its lanthanum chromite powder reveals that this company can supply suitable interconnect powders that meet the current requirements.

While SSC was not the second highest scorer, it was selected as secondary supplier for this material due to recent evaluations of its powder and the fact that it is a viable commercial supplier. HUA was the second highest scorer, but its inability to supply commercial quantities of powder reproducibly eliminated it from being a viable supplier.

4.5.6.3 Lanthanum Manganite

Primary: Trans-Tech
Secondary: None

The highest scorer was Trans-Tech. The manganite powder supplied by this company has proven to be as good as the HUA powder which has been used up to this time.

No single supplier has been selected to be the secondary supplier for this material. While HUA received the second highest point total, as was the case with the chromite powder HUA is not a viable commercial supplier of powders. Potential candidate suppliers for the secondary position include AlliedSignal at both Des Plaines and Morristown, Rhone-Poulenc, and SSC.

4.5.6.4 Nickelous Oxide

Primary: J.T. Baker
Secondary: Cerac

J.T. Baker and Cerac, primary and secondary suppliers respectively, were the only vendors found capable of supplying more than just research quantities of nickelous oxide in the required reagent grade. J.T. Baker, due to being the current supplier and having the cheapest price, was selected as primary supplier.

4.5.6.5 Anode Additive 1

Primary: Meller Optics

Secondary: ALCOA

Meller Optics, the current supplier of Anode Additive 1, was chosen as the primary supplier. Alcoa ranked second numerically but its low price makes it an extremely desirable candidate as primary supplier.

4.5.6.6 Binder

Primary: Union Carbide

Union Carbide was the only supplier contacted regarding the supply of this binder. The material is commercially available in bulk quantities and meets all of the current binder system requirements.

4.5.6.7 Plasticizer

Primary: Monsanto

The current supplier, Monsanto, was the only supplier of plasticizer contacted for this evaluation. The material is readily available in bulk and is priced at nearly half the METC1 cost study price.

4.5.6.8 Anode Additive 2

Primary: Cabot Corp.

Cabot Corp. was the only supplier contacted regarding the supply of this material for use as a possible additive in the anode formulation. This material is not used in the current batch formulation.

4.5.6.9 Pore Former

Primary: E M Science

E M Science, the current supplier of pore former, was the only vendor considered for this evaluation. Cheaper suppliers of this pore former undoubtedly exist; however, this material accounts for only 0.3 percent of the raw material costs and therefore an extensive search for an alternate supplier was not warranted.

4.5.7 Further Recommendations

During the course of this evaluation, it became apparent that several areas in the selection of commercial raw material suppliers should be given further consideration.

Recommendations for the areas that should be considered further are discussed below:

- (a) Lower purity zirconia should be considered from a cost standpoint if electrical and ionic properties are not negatively affected. Each coprecipitation step performed to achieve another percentage point in purity drives the cost up. Even a slight reduction in zirconia cost would have a substantial impact on the total production cost since zirconia accounts for 42 percent of the raw material cost.
- (b) Manganite and chromite materials utilizing mixed rare earth compounds instead of purified lanthanum should be considered from the standpoint of cost. The ore purified to obtain lanthanum is basically a mixture of many of the rare earth elements. The high price of lanthanum is driven by the cost to remove these other rare earths from the ore. If the cathode and interconnect could be produced from powders containing these mixed rare earths, the total raw material cost for producing a fuel cell would drop substantially. The manganite and chromite materials combined represent 52 percent of the total raw material cost.
- (c) Nickelous oxide of a different oxidation state should be evaluated for use in the anode on the basis of cost. Black nickelous oxide, which is a combination of NiO (approximately 77 wt percent) and other oxidation states can be obtained for 25 percent the cost of green nickelous oxide that is 99 wt. percent NiO. The change in oxidation state might not have any affect on the anode properties following reduction of the nickelous oxide to nickel.
- (d) A lower price grade of pore former could be identified and evaluated. This recommendation ranks low on the priority list since the total cost of the pore former accounts only for 0.3 percent of the total raw material cost.
- (e) Evaluation of a zirconia powder coated with nickelous oxide for the anode should be considered. Several suppliers indicated the ability to produce such a powder, which would provide a more homogeneous dispersion of nickel throughout the anode layer. A cost/benefit analysis would be required to determine whether the decrease in manufacturing cost would outweigh the increase in raw material cost. The most important consideration, of course, would be the effect on the electrochemical performance of the anode layer.

4.5.8 Conclusions

The evaluation described above concludes that commercial raw material suppliers exist who can be fully compliant with the anticipated material requirements in the foreseeable future to support the commercial manufacture of MSOFC's. Several of the identified raw materials that meet these anticipated requirements are currently available. Changes to the raw materials identified in this evaluation will most assuredly occur as the development process evolves and improvements are made. These raw material

changes could therefore affect the identification of material suppliers who are fully compliant with the anticipated material requirements.

This study revealed an estimated raw material cost to manufacture the MSOFC that falls nearly midway between the current and economic costs used in the METC1 manufacturing cost study. This cost level should not affect the financial viability of commercially manufacturing the MSOFC. Evaluations of lower purity materials should be performed that could substantially reduce the raw material cost of MSOFC manufacture.

4.6 MANIFOLD DESIGN AND DEVELOPMENT

In the early stages of the project, ASE adopted the manifolding technology developed by ANL for testing MSOFC stacks. An illustration of this stack manifolding technique is shown in Figure 4-40.

Preparation of the stacks is outlined below.

- (a) Obtain zirconia plate large enough to accommodate the fuel cell stack, plus the manifolding side bars, as well as sufficient material for side bars and top plate. Aremco 516 zirconia-based high-temperature cement is used to seal the porous zirconia plates, as well as to hold the manifold together.
- (b) Drill holes in the manifold base plate to accommodate gas inlet and outlet tubes, plus one hole in the center of both base and top plates to accommodate the current collectors.
- (c) Coat the surfaces of the base and top plates, which will be facing the fuel cell, with several thin coats of cement to make the plates gas-tight. A picture of the base plates, four-part top plates, and side bars is shown in Figure 4-41.
- (d) Apply metallizing layer of platinum paste to both sides of the fuel cell stack; fire to 800°C. When the stack cools, attach platinum screen current collectors with more platinum paste, and fire again to 800°C.
- (e) Attach the feeder tubes to the underside of the base plate and allow it to dry thoroughly.
- (f) Cement the fuel cell stack to the base plate. When dry, the edges of the stack are sealed with cement (on the fuel side, seal off the cathode material, and on the oxidizer side, seal off the anode material).
- (g) Cut the side bars to fit the height of the stack, and then seal the inner sides with cement. When dry, the side bars are cemented down and the corners of the stack are filled in with cement to prevent mixing between the fuel and oxidizer.
- (h) Install thermocouples in gas passages and cement down the top plate. Attach leads to current collectors and thermocouples. Connect the gas feed and exit tubes. The manifold stack assembly is heated to 1000°C. The stack is now ready for test.

Figure 4-40. Illustration of Stack Preparation

Figure 4-41. Sealed Base Plates, Top Plates, and Side Bars for MSOFC Manifolding

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Posttest and stress analysis showed that the original manifolding technique placed stresses on the stack due to its massive size and differences in thermal expansion of the manifold assembly and the stack. An alternative approach (see Figure 4-42) employed thin sections, formed from zirconia plates, to reduce stress on the stacks. The design provides manifolding for flowing hydrogen through the stack only. Although the manifold was easily formed by sealing the zirconia plates together with either "K" glass (obtained from ANL) or "S" glass (from Specialty Glass Company), significant difficulties were encountered in sealing the manifold to the stack. The nature of these difficulties is discussed in para. 3.6.

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F-68108

Figure 4-42. Thin-Plate Manifold

 

5. TESTING ON COAL GAS

The principal focus of the testing effort on this project was to help assess the root causes for the performance-shortfalls in the fabricated cells and stacks. The cell performance demonstrated that an excellent approach to cell construction was found. An analysis of the electrochemical performance data showed that the performance of cells using the thin-film electrolyte construction was truly superior, approaching 1 w per square centimeter at 1000°C.

Tests of multicell stacks at small-scale demonstrated a performance approaching that of the individual cells. However, as the stacks were scaled in footprint, significant performance shortfalls were observed. These shortfalls were caused by stress-induced structural defects. These defects were produced by differences in the thermal expansion characteristics of the components and changes in the dimensions of the anode and interconnect layers caused by the introduction of the hydrogen fuel. Additionally, it was found that the interconnect material substantially weakened when exposed to hydrogen. Moreover, a satisfactory sealant was not found, leading to a reduction in the open circuit voltage and causing damage to the electrode materials.

By modifying the stack design and properly selecting the anode and interconnect materials it was found possible to achieve a sufficiently good thermal expansion match that this source of stack defects was eliminated. Additionally, the effects of hydrogen on the anode were largely eliminated as a source of structural failure by modifying the composition of the anode.

5.1 TESTING FACILITIES AND THEIR OPERATION

There were two principal testing facilities used during the course of the project. They were located at ASE Space Laboratory Facilities in Torrance, California. Additionally, early testing was done at the Argonne National Laboratory facilities, primarily to familiarize ASE personnel with testing procedures.

With project funding, ASE has built a stack testing facility. The facility is capable of accommodating stacks up to 1 cu ft in volume in a top-loading Teresco furnace capable of operating at temperatures up to 1100°C. The facility can provide an inert gas and fuel to the fuel manifold, and inert gas and air or oxygen to the oxidant manifold while precisely controlling the individual flow rates from 0.03 to 100 standard liters per minute. The fuel line is equipped with a heated humidifier, pre- and poststack humidity analyzers, and a CO/CO₂ analyzer. Both lines are equipped with downstream mass flow meters.

The facility is provided with a high-current (to 100 amp) direct-current power supply (Hewlett Packard Model 6456B). It augments the emf produced by the stack in high-current operation to compensate for current lead voltage drops. An electronic load (Kikisui Model PLZ 100 3W) rated at 1000 w and 100 amp is provided to control the fuel cell stack circuit current.

Gas flow is computer controlled. Fuel and oxidant flow rates, fuel humidity level, inlet and outlet fuel and oxidant temperatures, fuel cell voltage and current, and effluent

oxygen, carbon monoxide, and carbon dioxide concentrations are displayed at the computer console.

The other ASE fuel cell test facility (Figure 5-1) is located in the ceramics fabrication facility. For evaluating electrochemical performance, a small fuel cell in the form of a disc is placed at the end of tubular gas manifold in a Lindbergh tube furnace, and the anode is exposed to hydrogen. Current and voltage of the cell are controlled with a PAR galvanostat/potentiostat and a Hewlett-Packard power supply. Ac impedance measurement equipment (Figure 5-2) is available to determine interfacial effects in cells and stacks. A Teresco top-loading furnace and gas supply system are available for testing small-scale stacks (up to 3-by-3-in. footprint). A high-current (to 60 amp) Hewlett-Packard Model 6032 A power supply and two electronic loads (Kikisui Model PLZ152WA) capable of controlling up to 30 amp individually and 60 amp operating in parallel, are available. A similar facility for testing small-scale stacks is available at ANL.

5.2 CELL TESTING

The standard means of testing the cells were to obtain polarization curves for 1-in.-dia discs inserted in a single-cell test apparatus. The principal objectives of the tests were to assess the effects of changes in fuel cell materials, processing approaches and layer thickness ratios on the performance of the fuel cells and to form a performance baseline for assessing stack performance.

Figure 5-1. Fuel Cell Test Facility

Figure 5-2. Ac Impedance System

F-66385

5.2.1 Single-Cell Test Apparatus

The single-cell performance tests were conducted with an apparatus such as that shown in Figure 5-3. The single cell test apparatus is shown schematically in Figure 5-4. The apparatus consists of an outer alumina (or quartz) tube containing oxidant gas. A smaller gastight alumina tube is placed inside the outer tube. A single-cell sample is cemented to the end of the zirconia tube. Platinum wires are attached to the cell for electrical connections. Connections from platinum wires to the sample are made with a platinum paste. This connecting method has the advantage of not placing any undue mechanical stress on the thin ceramic layer. A gas flow control and manifold system supplies the apparatus with gas of various compositions and flow rates.

5.2.2 Test Results

Initial single-cell tests focused on determining the electrochemical performance of cells with the 2:1:1 A:E:C construction and comparing it to the previous 1:5:1 construction. Additionally, the effects of different processing techniques, current collection technology, and sealing technology were evaluated. With the advent of the thin-film electrolyte technology the electrochemical performance of that construction and its variations were also evaluated.

A single disc of 2:1:1 construction was tested to establish its performance baseline. The cell had an open circuit voltage of 1.06 v. It was run for approximately 100 hr under no-load conditions and then under load for an additional 100 hr. In each case,

F-58288

Figure 5-3. Fuel Cell Ready for Test

Figure 5-4. MSOFC Single-Cell Test Apparatus

there was no observable drop in operating voltage. The area-specific resistance of the cell was slightly less than 0.7 ohm-centimeters squared, comparable to cells of the 1:5:1 construction.

Three cells of 2:1:1 construction were tested to determine the effects of attritor-milled vs ball-milled anode processing.

The single cells were designated SC1351M, SC1352A, and SC1353A. The cells had an anode/electrolyte/cathode-electrolyte intermediate (A/E/CE) layer thickness ratio of 2:1:1. The anodes in cells SC1351 and SC1353 were fabricated using attritor-milled NiO, whereas the NiO in the anode for cell SC1352 was ball milled. The cells were heated to 1000°C under flowing He before testing began. Initially, 10 ccm of H₂ was used to reduce the NiO to Ni. The open-circuit voltage (OCV) on all three cells was stable at 1.05 v. Cell SC1351 was initially tested after reduction of the NiO (see performance curve in Figure 5-5). The second test was conducted after a load of 100 ma/cm² had been applied for 50 hr. The OCV was inexplicably higher (1.07 v) for this second test. The area-specific resistance (ASR) of cell SC1351 is 0.7 ohm-cm².

The initial performance curves for cells SC1352 and SC1353 are shown in Figure 5-6. The anode in cell SC1352 contains ball-milled NiO, whereas the anode in cell SC1353 contains attritor-milled NiO. Although these results are preliminary and have not yet been repeated, a slight difference appears to exist in the ASR of the two cells. Cell SC1353, with the attritor-milled NiO, has the lower ASR (0.7 ohm-cm²) and better performance.

SC1351 M; T=1000°C

Figure 5-5. Polarization Curves for Single-Cell SC1351 at 1000°C with Air as Oxidant and H₂ as Fuel

Figure 5-6. Polarization Curves for Single Cells SC1352 and SC1353 at 1000°C with Anodes Prepared with Ball-Milled and Attritor-Milled NiO

A series of three performance curves for cell SC1353 is shown in Figure 5-7. One was measured initially after reduction of the NiO; a second was measured after loading at 100 ma/cm² for 36 hr, and the third after loading at 250 ma/cm² for 96 hr. There is little difference in the performance of the cell as a function of time at either of the loads. The ASR of the cell varies from 0.6 to 0.7 ohm-cm², comparable to cell SC1351.

Two cells were fabricated with baseline anode and electrolyte layers and an alumina-toughened cathode-electrolyte layer.

- Cell ED065-8—Single-cell ED065-8 was fabricated with baseline anode and electrolyte layers and an Al₂O₃-toughened cathode-electrolyte layer, using a 2:1:1 (A:E:CE thickness ratio) construction. The initial performance curve for ED065-8 is shown in Figure 5-8. The OCV was stable at 1.01 v. The initial ASR was 1.2 ohm-cm². This ASR is slightly higher than the typical value of 0.7 to 1.0 ohm-cm² obtained for strictly baseline 2:1:1 single cells.
- Cell ED065-7—This cell contained baseline A, baseline E, and alumina-modified CE. The cell construction was a 2:1:1 layer thickness ratio. The cell polarization curve is shown in Figure 5-9. The observed open circuit voltage (OCV) under those conditions was 1.046 v, close to the theoretical value of 1.055 v. The area specific resistance (ASR) of the cell calculated from the slope of the polarization curve was about 1 ohm-cm². Based on this result, it appears that the electrochemical performance of alumina-modified CE is comparable to that of baseline CE.

The cell was operated under 250 ma/cm² load for about 170 hours. The operation was inadvertently terminated due to brief power loss in the laboratory test area. The initial cell voltage under the load was 0.69 v and the final cell voltage was 0.53 v. During the load operation period, the OCV decreased about 60 mv. After testing, visual examination of the cell showed debonding or dewetting of the seal material on the cathode surface. This might allow small gas cross leakage in the cell, causing performance degradation during the life test.

- Cell ED040-08—This cell was also a baseline cell of 2:1:1 construction. The initial OCV was 1.05 v and the ASR of the cell (obtained from the cell polarization curve) was 0.8 ohm-cm². A long-term load test (250 ma/cm²) was performed on the cell. The results are summarized below.

A long-term load test was performed on one of the baseline formulation single cells.

Cell 1353A

Figure 5-7. Effect of Operation Time on Polarization Curves for Single Cell SC1353 at 1000°C

Figure 5-8. Polarization Curve of Cell ED065-06,
Temperature = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

Figure 5-9. Polarization Curve of Cell ED065-07
Temperature = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

<u>Time, hr</u>	<u>Cell Voltage, v</u>	<u>Open Circuit Voltage, v</u>
0	0.85	1.05
64	0.79	0.99
138	0.76	0.97
165	0.75	0.96
264	0.68	0.95
310	0.66	0.94

This long-term test was terminated after 310 hr. The post-test analysis indicated there was a small leak in the seal material. This explained the slow degradation of the OCV and cell voltage with time.

Since the present platinum paste method is unreliable and time-consuming, two alternate methods to attach current collectors were evaluated. Both methods involved applying current collectors to single cells using the same materials utilized in multicell stack bonding. The first method involved dissolving anode and cathode bonding tapes in alcohol to form a slurry. The slurry of each electrode material was then used to apply current collectors to the appropriate electrode surfaces of single cells. Single cells ED045-26, ED040-45 and ED040-36 were prepared in the manner discussed above and performance tests were conducted on each cell. Each of the cells was fabricated from baseline materials and constructed with an A:E:CE layer thickness ratio of 2:1:1. The cells were heated to 1000°C under helium before testing commenced. Performance tests were conducted at 1000°C with 97 percent H₂/3 percent H₂O as fuel, and air as oxidant. The test results are summarized below:

- ED045-26—During initial performance testing, severe voltage instabilities occurred at a current of 500 ma. The sample was allowed to stabilize for 48 hr, and a performance test was performed without voltage instabilities. The performance curve for ED045-26 is presented in Figure 5-10. The ASR obtained was 0.96 ohm-cm². The OCV was stable at 1.05 v.
- ED040-45—During performance testing, severe voltage instabilities were experienced at a current of 50 ma. The polarity was reversed at 400 ma for 20 sec in an attempt to improve performance. However, voltage instabilities were encountered at 100 ma. The OCV was stable at 1.02 v.
- ED040-36—Voltage instabilities occurred at 50 ma during performance testing. The voltage instability was overcome by performing an electrolysis at 800 ma for approximately 5 min. Figure 5-11 shows the polarization curve generated after reverse polarization. The resulting ASR was 1.4 ohm-cm². The OCV was stable at 0.98 v.

An additional method was evaluated to attach current collectors to cells which involved adding platinum powder to the slurry mixtures of each of the electrode materials. The slurry/Pt powder was mixed until a homogeneous mixture resulted.

Figure 5-10. Performance Curve of Cell ED045-26
 T = 1000°C, Fuel = 98% H₂/3% H₂O, Oxidant = Air

Figure 5-11. Performance Curve of Cell ED040-36 After Electrolysis at 0.8 amp for 5 min: T = 1000°C, Fuel = 97% H₂/3% H₂O, Oxidant = Air

Current collectors were attached to the electrode surfaces of the single-cell ED040-35 using the slurry/Pt mixture. Single-cell ED040-35 was prepared using this method and a performance test was conducted. Performance testing was performed with the conditions mentioned earlier. The results are presented below.

- ED040-35—Voltage instabilities were encountered at 400 ma during performance testing. The sample was allowed to stabilize overnight under H₂; however, voltage instabilities still persisted at 400 ma. The OCV was stable at 1.015 v.

One possible reason for the voltage instabilities observed during performance testing appears to be a poor contact between the platinum screen current collector and the electrode surface. Therefore, the present current collector application method continues to be used for single-cell testing.

Platinum screen current collectors are applied to single-cell samples using the standard platinum paste method. However, it was determined that increasing the metallizing temperature (from 800° to 900°C) minimizes the problems of current collector detachment encountered in the past.

FiberFrax LDS moldable insulation caulk was evaluated as a candidate to provide a removable (noncement) material for sealing single-cell discs for performance testing.

- ED040-4—This single cell was prepared for testing and applied to the test rig using LDS moldable caulk as a sealant. The initial OCV obtained for FD040-4 (with 97 percent H₂/3 percent H₂O as fuel, and air as oxidant) was 0.85 v. This OCV is lower than the typical value of 1.05 to 1.07 v obtained for single cells. A performance test was not performed due to a slow degradation of the OCV over time, indicating the presence of a significant leak. Upon observation of FD040-4 after cooling to room temperature, large gaps between the LDS moldable material and the single cell were observed.

A performance test was performed on a single cell with the anode modified to improve its thermal expansion coefficient match. The objective of the test was to evaluate the effect of the modification on anode, thus cell, performance. The test was carried out at 1000°C with humidified hydrogen as fuel, and air as oxidant. The open-circuit voltage (OCV) of the cell was 1.06 v, and the area-specific resistance (ASR) of the cell was 0.8 ohm-cm². This ASR was consistent with the performance expected for cells with baseline anodes. Thus, it appeared that the modification had no significant effects on the anode performance.

A thin-electrolyte cell (EE388-03) was tested over the temperature range of 700° to 1100°C with humidified hydrogen fuel and air oxidant. The performance curves of the cell are shown in Figure 5-12. The cell exhibited excellent open-circuit voltages (OCV's) and low area specific resistances (ASR's), as summarized in Table 5-1.

Figure 5-12. Performance Curves of Thin-Electrolyte Cell
Fuel = Humidified Hydrogen (3% H₂O), Oxidant = Air

TABLE 5-1		
PERFORMANCE OF THIN-ELECTROLYTE CELL		
Temperature, °C	OCV, v	ASR, ohm-cm ²
700	1.11	1.91
800	1.10	0.67
900	1.09	0.43
1000	1.05	0.35
1100	0.97	0.37

Examination of the cell after the test showed no cracking in the dense electrolyte, and good bonding between the thin electrolyte and electrode layers (Figure 5-13).

Performance testing was carried out on several cells fabricated by cofiring anode/thin electrolyte bilayer at 1400°C, followed by applying the cathode and firing at 1250°C. Performance tests were conducted over the temperature range of 600° to 1100°C with humidified hydrogen fuel and air oxidant. The results of each single-cell test are given below.

Figure 5-13. SEM Micrograph of Thin-electrolyte Cell After Testing

5.2.3 Cell EE388-04

The performance curves of the cell are shown in Figure 5-14. The cell exhibited excellent open-circuit voltages (OCV's) and low area-specific resistances (ASR's), as summarized in Table 5-2. High power densities were obtained with this cell, e.g., 0.55 w/cm² at 800°C and 0.91 w/cm² at 1000°C.

5.2.4 Cell EE424-01

The cell, EE424-01, was fabricated using the same batches as EE388-04 but was thermal cycled up to the bonding temperature (1250°C) before the test. The purposes of this test were to assess the effect, if any, of the bonding process on cell performance and to obtain a performance baseline for stack testing. The performance of EE424-01 is summarized in Table 5-3, and the polarization curves are shown in Figure 5-15. The cell exhibited good open-circuit voltages at the test temperatures. The data show an approximate 10 percent increase in ASR at 800°C, and an approximate 20 to 25 percent increase in ASR at 1000°C as compared to the average of uncycled cells. This phenomenon could be due to increased manganese migration from the cathode, more lanthanum zirconate formation at the interface, or electrode microstructure change in the cycled cell.

Figure 5-14. Voltage Current Curves for Cell EE388-04
Obtained at Different Temperatures

TABLE 5-2		
PERFORMANCE OF THIN-ELECTROLYTE CELL EE388-04		
Temperature, °C	OCV, v	ASR, ohm-cm ²
700	1.08	1.01
800	1.10	0.57
900	1.08	0.37
1000	1.04	0.30
1100	0.97	0.26

TABLE 5-3		
PERFORMANCE OF THIN-ELECTROLYTE CELL EE424-01		
Temperature, °C	OCV, v	ASR, ohm-cm ²
700	1.08	1.36
800	1.09	0.68
900	1.06	0.44
1000	1.00	0.48

Figure 5-15. Polarization Curves of Cell 424-01

In addition to the testing using standard gas compositions and flow rates, cell EE424-01 was also tested under conditions of lower hydrogen contents and flow rates. The tests, carried out at 700°C, were performed to assess the effect of hydrogen concentration and flow rate on cell performance in single-cell test procedures. The results indicate that there was no significant change in either OCV or ASR with the different fuel gas compositions and flow rates used (Table 5-4).

TABLE 5-4			
PERFORMANCE OF CELL EE424-01 AT 700°C WITH DIFFERENT FUEL GAS COMPOSITIONS AND FLOW RATES			
Gas Mixture	Flow Rate, sccm	OCV, v	ASR, ohm-cm ²
97% H ₂ /3% H ₂ O	5.0	1.08	1.40
97% H ₂ /3% H ₂ O	10.0	1.10	1.43
14.6% H ₂ /82.4% He/3% H ₂ O	5.0	1.05	1.52

5.2.5 Cell EE472-15

Cell EE472-15 was fabricated using electrolyte made with as-received zirconia. This cell was tested with a different test procedure. In the other cell tests, the single cell was reduced at the lowest temperature tested (600° or 700°C), and then the cell would be heated to obtain polarization curves at higher temperatures. Cell EE472-15 was reduced at 1000°C, and then cooled to obtain polarization curves at temperatures below 1000°C. The performance of EE472-15 is summarized in Table 5-5 and the voltage/current curves are shown in Figure 5-16.

5.2.6 Cell EE408-02

In addition to the polarization test, the performance tests on cell EE408-02 included ac impedance measurements. Figure 5-17 shows an example of ac impedance curves obtained at different temperatures. The results of the performance tests for cell EE408-02 are summarized in Table 5-6.

TABLE 5-5		
PERFORMANCE OF THIN-ELECTROLYTE CELL EE472-15		
Temperature, °C	OCV, v	ASR, ohm-cm ²
800	1.01	0.85
900	1.02	0.59
1000	1.02	0.38

Figure 5-16. Voltage/Current Curves at Different Temperatures of Cell EE472-15

Figure 5-17. Ac Impedance Curves for Cell 408-02 Obtained at Different Temperatures

TABLE 5-6					
PERFORMANCE OF SINGLE CELL EE408-02					
Temperature, °C	OCV, v	ASR, ohm-cm ²			
		Total*	Total**	Bulk**	Interfacial**
615	0.48	0.82	1.03	0.27	0.76
711	0.97	0.94	1.63	0.17	1.46
805	1.01	0.52	0.80	0.13	0.67
902	0.98	0.32	0.49	0.10	0.39
1011	0.94	0.25	0.25	0.08	0.17
* Calculated from polarization plots					
** Calculated from ac impedance curves					

In this table, the total cell ASR has been calculated from both the polarization plots and ac impedance curves. Ac impedance measurements were performed on the cell before and after each polarization curve. The data for 805°, 902°, and 1011°C were collected in the first 14 hr after heating the cell to 1000°C, whereas the 711° and 615°C data were collected after 79 and 96 hr, respectively. The low OCV observed at 615°C indicates that there was degradation, probably of the seal, over the 96-hr test period. At all temperatures, the bulk ASR is higher than expected from the conductivity of the thin-electrolyte layer. For example, at 1011°C the bulk ASR is 19 times the expected value. The reasons for this are not known at present. The interfacial ASR at 1011°C (0.17 ohm-cm²) is approximately what is expected from the kinetics of charge transfer and diffusion observed in the past for this system.

5.2.7 4x4-in. Single-Cell Plate

The electrochemical performance of a 4x4-in. anode/thin-electrolyte/cathode plate was assessed using Pt foil current collectors. The test was performed at 1000°C with humidified H₂ as fuel and air as oxidant. The polarization curve for the cell is shown in Figure 5-18. The maximum OCV exhibited by the cell was 0.90 v. The ASR of the cell was 3.19 ohm-cm². The cell lost all OCV at the operating temperature after only 18 hr. The sudden loss of OCV was believed to be caused by the cell fracturing. (After the cell was cooled to room temperature, it was seen to be severely fractured.) In addition, the fragments of the cell showed significant bowing and deformation. This observed deformation has been found to be caused by the anode reduction and oxidation.

Two tests were made with thin-film electrolyte cells in which the cathode was cofired with the anode and electrolyte.

Thin-film electrolyte cells were fabricated with modified anode formulations developed to reduce the anode shrinkage observed when hydrogen was introduced to the cell.

B-26830

Figure 5-18. Polarization Curve for a 4x4-in. Cell with Pt Foil Current Collectors

- (a) Cell EE 480-01: This cell was made with cofired cathode layer. The fabrication involved forming green anode/thin-electrolyte bilayer, applying cathode on the green bilayer, and cosintering the cell. This cell showed poor performance, with an OCV of only 0.9 v. Posttest examination indicated possible gas cross leakage through the cement seal.
- (b) Cell EE488-02: This cell was also made with cofired cathode. With humidified hydrogen as fuel and air as oxidant, the observed OCV was 0.99 v. This cell also displayed poor performance. From posttest analysis, hairline cracks in the cell appeared to be the reason for the observed poor performance.
- (c) Cell EE536-02: This thin-electrolyte single cell contained a modified anode (formulation 2). This cell showed good OCV and performance close to that of the standard anode formulation. Polarization curves for this cell, as well as the power density as a function of current density, are shown in Figure 5-19. The ASR's of the cell were about 0.32 ohm-cm² at 1000°C and 0.70 ohm-cm² at 800°C. Therefore, it appears that the performance of the modified anode is comparable to that of the baseline.
- (d) Cell EE536-03: This single cell was a thin-electrolyte cell with a NiAl₂O₄-containing anode and a Sr-doped LaMnO₃ cathode. The objective of this test was to confirm the performance test results on cell EE536-02 (see April to June 1993 quarterly status report). When the anode side of the cell was

Figure 5-19. Voltage/Current and Power Density/Current Curves of Cell EE536-02
 Fuel = 97% H₂/3% H₂O, Oxidant = Air
 (Data for 1000°C with circle symbols taken with longer equilibrating time at applied current.)

exposed to hydrogen flow, the OCV increased to 0.65 v, then quickly dropped to about 0.32 v. A decrease in hydrogen flow increased the cell OCV, indicating possible cross-leakage. Because of the low OCV, no polarization experiments were performed. Posttest examination showed evidence of cracks in the seal. This explained the low OCV observed for the cell during the test.

- (e) Cell EI001-1: This thin-electrolyte cell was made with an anode containing lanthanum zirconate. At 1000°C, the cell OCV was 1.00 v, and the ASR was 2.7 ohm-cm². The ASR increased to about 14.8 ohm-cm² at 800°C, with an OCV of 1.05 v. It appears that the addition of lanthanum zirconate to the anode formulation causes cell electrochemical performance to degrade.
- (f) Cell EI001-2: This cell was tested to confirm the results on cell EI001-1. The cell showed an OCV of 1.01 v, and the ASR calculated from the polarization data was 2.5 ohm-cm², similar to that obtained for EI001-1.
- (g) Cell EI002-1: This thin-electrolyte cell contained an anode made with 6 mol% yttria-stabilized zirconia (6Y-ZrO₂). The cell showed an OCV of about 0.97 v. The ASR was unexpectedly high (1.7 ohm-cm²). After the test, the cathode current collector was found to detach from the cell. This detachment explained the high ASR of this cell.
- (h) Cell GI002-1: The anode of this cell was made from a mixture of NiO and mixed conducting TiO₂-YSZ. In this anode, Ti-YSZ replaced YSZ in the anode formulation. The polarization curves obtained at different temperatures are shown in Figure 5-20. This cell showed excellent performance, e.g., an ASR of 0.29 ohm-cm² at 1000°C, although the OCV's were somewhat lower than the theoretical values. It is not clear at present whether these low OCV's are caused by cross-leakage or by the presence of electronic conductivity due to the migration of titanium into the electrolyte during fabrication.
- (i) Cell EI002-2: The composition of this cell was the same as that of cell EI002-1. Figure 5-21 shows the polarization curves of the cell at different temperatures. The performance of the cell at 996° and 800°C is similar to that of baseline cells. This cell, however, showed low OCV and poor performance at 683°C. This poor performance was probably due to some kind of degradation of the cell after the high-temperature tests.
- (j) Cell EI005-1: This cell contained a 6Y-ZrO₂ anode. The polarization curves of the cell are shown in Figure 5-22. The ASR's of the cell were 0.35 ohm-cm² at 995°C and 0.98 ohm-cm² at 785°C. This confirms the results obtained for cell EI002-2, of similar composition.

The performance of a single-cell disk, E1011-5, was tested using Ag/Pd paste for current collector attachment (instead of platinum paste). The disc was a thin-electrolyte cell made with 6YSZ anode. The objectives of this test were to establish a performance

B-28286

Figure 5-20. Polarization Curves of Single Cell GI002-1 Containing Ti-YSZ Anode

B-28287

Figure 5-21. Polarization Curves of Single Cell EGI002-2, Having 6Y-ZrO₂ Anode

Figure 5-22. Polarization Curves of Cell EI005-1, Having 6Y-ZrO₂ Anode

baseline for stack testing and to determine the effect, if any, of Ag/Pd paste on cell performance. The cell polarization curve (obtained with hydrogen fuel and air) is shown in Figure 5-23. The best-fit straight line for the experimental data gives an area-specific resistance (ASR) of about 0.57 ohm-cm² for the cell. This value is somewhat higher than the ASR of about 0.35 ohm-cm² for similar cells with platinum paste attachment. The higher ASR for this cell was mainly caused by the higher voltage drop at low current density (<0.1 amp/cm²). In theory, voltage losses at low current densities are due to activation overpotential. It could be that Ag/Pd paste affects the electrochemical reaction kinetics. Further testing is required to confirm this.

5.3 STACK TESTING

The stacks were tested in the METC 2 test facility, described in para. 5.1, using the manifolding technology discussed in para. 4.6. Both single-cell "stacks" and multicell stacks were tested. The results are discussed below.

5.3.1 Single-Cell Stack Testing

During the course of the project a great number of single-cell stacks were tested. Initially, these stacks had a 1:5:1 A:E:C cell construction and poor electrochemical performance. Improvements in performance occurred with the 2:1:1 cell construction, better bonding processes, and better sealing techniques. A record of these improvements is shown in Figure 5-24.

Figure 5-23. Polarization Curve of Cell E1011-5

Figure 5-24. Improvement in Single-Cell Stack Performance

This shows the best stack performance as of the date given. The tests associated with the performance milestones displayed in the figure are described below.

During December 1990 two stacks (ST 1085 AND ST1217) with a footprint of 1.25 in. and a 1:5:1 cell construction were tested. Both stacks showed an OCV of 0.9 v and a very low ASR of 53 ohm-centimeters squared.

During January 1991 two stacks (ST1083 and ST1084) were tested. Both had 1-in. footprints and 1:5:1 cell construction. Stack ST1084 showed an ASR of 8.1 ohm-centimeters squared. Stack 1083 showed an ASR of 9.1 ohm-centimeters squared. The performance of this stack as a function of temperatures ranging from 800° to 1000°C is shown in Figure 5-25.

During May 1991 two stacks (ST1417 and ST1432) with a footprint of 1 in. and a 2:1:1 cell construction were tested. Both stacks exhibited an ASR of 2 ohm-centimeters squared. ST1417 had an OCV of 0.860 v while ST1432 had an OCV of 0.906 v. ST1432 was kept intact and retested one week later, showing an OCV of 0.825 v and an ASR of 4.1 ohm-centimeters squared.

In August 1991 stack EB019-2 with a 1-in. footprint and a 2:1:1 cell construction demonstrated an ASR of 1.53 ohm-centimeters squared with an OCV of 0.89 v. Following this test, the single-cell stack testing was terminated and efforts were focused on improving the performance of multicell stacks.

5.3.2 Multicell Stack Testing

In September 1990 ASE and ANL personnel tested a two-cell stack at ANL's laboratories. Stack ST1207 consisted of two single-cell modules (1:5:1 cell construction) bonded to an interconnect and top and bottom electrode plates with a platinum slurry bonding formulation.

The manifolded stack (ST1207) was heated to 1000°C, while flowing a low purge flow of helium on the fuel side and clean, dry, bottled air on the oxidizer side. When the stack reached operating temperature, the fuel side was subjected to 5% H₂/95% He (water saturated) and checked the open circuit voltage. For safety reasons, a weak H₂ mixture is used when checking a cell for the first time at temperature. Open circuit voltage (OCV) under that mix was found to be 1.45 v (theoretical is 1.8 v), indicating reasonably sound interconnect and electrolyte structures.

The flow through the fuel side of the stack was then changed to a mixture of approximately 50% H₂/50% He (water saturated). An OCV of 1.85 v was achieved (theoretical is 2.1 v). The current was then increased by increments of approximately 0.15 amp. At a current of 1.00 amp, a voltage of 1.06 v was measured (indicating 1.06 w of power). After this point, the voltage dropped dramatically. It is suspected that the interconnect-cathode bond weakened, increasing cell internal resistance.

Dimensions of the stack ST1207 were: total height of 0.25 in., length of each side of 1.75 in., "active" area was estimated to be 1.5 in. by 1.5 in. Total flow rate through

Figure 5-25. Performance of ASE MSOFC Stack ST1083

the fuel side was 510 std ml/min. Airflow was 900 std ml/min. Operating temperature was 1000°C.

Although the performance of the stack was encouraging the bonding technology was not sufficiently robust for handling and effective testing and this bonding construction was abandoned.

Subsequent tests were conducted with ceramic bonds until the latter stages of the project were reached, when silver-palladium bonds were used with the plate-and-bar construction.

Many multicell stacks were tested. As with the single-cell stacks these stacks had a 1:5:1 A:E:C cell construction and poor electrochemical performance. Improvements in performance occurred with the 2:1:1 cell construction, better bonding processes, and better sealing techniques. A record of these improvements is shown in Figure 5-26.

This shows the best stack performance as of the date given. The tests associated with the performance milestones displayed in the figure are described below.

During May 1991 a ceramic-bonded two-cell stack with construction similar to single-cell stacks ST1417 and ST1432 with a footprint of 1 in. and a 2:1:1 cell construction was tested. An OCV of 1.55 v with a per-cell ASR of 40 ohm-centimeters squared was achieved.

Two-cell stack EG259-02 was tested in December 1991. In an attempt to eliminate external variables during performance testing, an alternate manifolding procedure was utilized for the testing of EG259-02. The alterations involved prefiring a majority of the manifold components using Aremco 516 zirconia-based cement before the stack was inserted into the manifold. The stack was then inserted into the manifold and sealed using Aremco 571 magnesia-based cement. The 516 cement was not used to seal the stack in the manifold since it was determined that it may induce cracks in the stack as a result of expansion during curing. The stack's OCV was 1.527 v, and the ASR was 15.94 ohm-cm² (7.97 ohm-cm² per cell).

During June 1992 a two-cell stack of similar construction to those above was tested using glass sealants.

The observed maximum OCV was 1.80 v for two-cell stack EE344-03. The stack showed an ASR of 2.5 ohm-cm² per cell. Four additional electrochemical performance curves were generated for EE344-03 at 800°, 900°, 1000°, and 1050°C. The results are shown in Figure 5-27. As expected, the OCV degraded slightly with increasing temperature and the ASR decreased with increasing temperature. Stack EE344-03 was cooled to room temperature and heated back to 1000°C to evaluate thermal cyclability. The OCV recovered successfully, however the ASR degraded to 3.4 ohm-cm² per cell.

During July 1992 two-cell stack EE355-4 achieved the best electrochemical performance of all stacks tested during the project. The per-cell ASR of the stack was 1.0 ohm-centimeters squared with an OCV of 1.74 v. The stack produced 1.0 w of power.

— TWO-CELL STACK
 - - - FOUR-CELL STACK

IG-11877
 8-19-92

Figure 5-26. Improvements in Bonding and Manifolding Have Led to Major Gains in the Performance of Multicell Stacks

IG-14282

Figure 5-27. Polarization Curves for Stack EE344-03 as a Function of Temperature

Four-cell stack EE377-1, tested in August 1992, had an initial OCV of 3.61 v and an ASR of 2.5 ohm-centimeters squared per cell. This stack also produced 1 w of power.

Following this successful sequence of tests with 1-in. footprint stacks, several attempts were made to fabricate larger footprint modules to scale the stacks to the 100-w power level. Significant difficulties were encountered in scaling the single-cell modules to the larger footprints required for the construction of the high-power stacks. A decision was made to change to the plate and bar construction with thin-film electrolyte cells because of the success achieved with large footprint construction of these cells. Based on this construction, several three-cell stacks were assembled and tested.

- (a) Interconnect stack: The interconnect stack was attached to the zirconia manifolds using Material K glass as sealant. The manifolded stack was placed in the top-loading furnace in the stack test facility, electrical and gas connections were made, and the stack was then heated to 1000°C. Because one of the gas inlet tubes dropped off the manifold, no gas flow testing was performed. The stack was cooled to room temperature. Visual examination of the stack showed a number of cracks in the manifold plates, especially the top plates. The cracks appeared to originate in the corners where the top and side manifold plates met. The glass did not appear to make good seals between the zirconia and the interconnect. No cracking or delamination was observed in the stack.
- (b) Three-cell stack: The stack was sealed to two zirconia manifold "ducts" on the fuel sides of the stack. Gas inlet and outlet tubes were attached to the duct bottom plates with Material K glass. Zirconia felt, impregnated with Material K glass, was used in the stack-to-manifold sealing. The stack was then placed in the test furnace with appropriate electrical and gas connections (Figure 5-28). The test setup was heated to 1080°C and held for 4 hr (to achieve stack-to-manifold sealing) under helium flow. The temperature was then reduced to 1000°C. During equipment check at temperature, the gas outlet tube fell off. One of the inlets also fell out. Resistance measurements indicated that the stack was shorted. The stack was then cooled to room temperature. Because of the problem with the inlet gas tube, no hydrogen was introduced into the stack.

Posttest examination of the stack indicated several cracks in the top manifold plates and one crack in one of the bottom plates. The cracks on the top plates appeared to originate from the corner where the side manifold plate and top manifold plate met. These cracks probably occurred during cooldown. The manifold seals looked all right, although possible glass "de-wetting" was observed at interconnect/manifold sealing areas. The stack showed no visible damage, indicating that the stack could be manifolded and thermal cycled with minimum cracking or delamination.

In October 1993 a three-cell stack was tested.

F-67565

Figure 5-28. Manifolded Three-cell Stack with Electrical and Gas Connections

The three-cell stack was sealed to two zirconia manifold ducts on the fuel sides of the stack. Gas inlet and outlet tubes were attached to the duct bottom plates with K glass. Zirconia felt, impregnated with the glass, was used in the stack-to-manifold sealing. The stack was then placed in the test furnace with appropriate electrical and gas connections. The test setup was heated to about 1080°C (to achieve stack-to-manifold sealing) under helium flow. The temperature was then reduced to about 1000°C.

At the test temperature with 3 l/min air flow and 0.5 l/min helium flow, the cell showed a voltage of about 0.015 v. This voltage increased to about 0.030 v when the helium flow rate increased to 3 l/min. Hydrogen was then introduced into the helium flow. At 0.5 l/min of 5% H₂-95% He, the cell voltage remained at about 0.014 v. The voltage was somewhat higher (about 0.090 v) at a flow rate of 3 l/min. Increasing the percentage of hydrogen increased cell voltage. At 30 percent H₂-70 percent He (3 l/min), the observed voltage was 0.216 v. This low open-circuit voltage for the three-cell stack, however, indicated significant gas leakage. The stack was held overnight at 30 percent hydrogen flow, when a power outage shut down the test. It should be noted that throughout test, no gas flow was detected at the gas outlet. Preliminary examination of the stack after the test showed significant interactions between the sealant and the interconnect, causing warpage of the interconnect cover plates.

During November 1993 off-line tests were conducted on a 4 x 4-in., three-cell stack utilizing S-glass (produced by Specialty Glass) at the stack-to-manifold interfaces. The three-cell stack comprised cells and fuel-side bars made from titanium-based anode formulation and interconnect plates and oxidant-side bars made from the

Ca,Co-doped LaCrO_3 formulation. The three-cell stack was sealed to two zirconia manifold ducts on the fuel sides of the stack. Gas inlet and outlet tubes were attached to the duct bottom plates with K-glass. Zirconia felt, impregnated with S-glass, was used in the stack-to-manifold sealing. The stack was then placed in the test furnace with appropriate electrical and mechanical connections. The test setup was heated to about 1000°C in an air atmosphere.

At the test temperature various flow rates of air, from 0.5 to above 5.0 l/min, were pumped into the fuel side of the stack. There was no evidence of outlet flow at any of the inlet flow rate conditions. The stack was then cooled and removed from the test assembly. Inspection revealed that the S-glass had flowed at temperature more than anticipated, creating gaps between the stack and manifold which allowed for leakage. Samples of the S-glass on the interconnect, at the interface, were analyzed. Preliminary results indicate that silica was removed from the glass during interaction with the interconnect. The removal of silica would lower the melting temperature of the glass, allowing it to be much less viscous at 1000°C than expected.

Based on these results and other off-line development tests, a preliminary investigation was begun on a buffer zone concept, which would shield the interconnect from the sealant, preventing interaction.

During December 1993 two off-line tests were conducted on the 6YSZ three-cell stack. Although the 6YSZ stack cracked during fabrication, it was still used for stack-to-manifold sealant tests.

The November 1993 status report stated that the S-glass (produced by Specialty Glass) was found to react with the interconnect plate and the zirconia felt at the operating temperature of 1000°C . In the first test using the 6YSZ stack, an attempt was made to prevent this reaction by bonding buffer strips of magnesium aluminum oxide with AgPd to the anode and cathode faces that would be in contact with the manifold. The stack was fired to 1100°C for 1 hr at a rate of $120^\circ\text{C}/\text{hour}$. The magnesium aluminum oxide strips cracked in many places, but the 6YSZ stack remained intact.

The second test determined the quality of the S-glass seal to the buffer strips and the manifold. It also compared the ability of S-glass and K-glass to seal the sides of the stack to the manifold with zirconia felt.

A bead of S-glass was used to seal the magnesium aluminum oxide strips on the top and bottom of the stack to the two manifolds. The sides of the fuel inlet manifold were filled with zirconia felt and S-glass, and the sides of the fuel outlet manifold were filled with zirconia felt and K-glass. The stack and manifold assembly was heated in a furnace to 1000°C for 1 hr at a rate of $180^\circ\text{C}/\text{hour}$. The top and bottom regions of the stack appeared well sealed to the manifold, and no adverse reactions were apparent. The sides of the fuel inlet manifold were completely open. The S-glass and zirconia felt reacted to form a low-viscosity glass which did not fill the side gaps. Figure 5-29 shows a photograph of the fuel inlet manifold after firing. The side was sealed with S-glass and zirconia felt, and the top edge was sealed with S-glass and magnesium aluminum oxide strips.

F-66387

Figure 5-29. Photograph of the Fuel Inlet Manifold After Firing. The Side Was Sealed with S-glass and Zirconia Felt, and the Top Edge Was Sealed with S-glass and Magnesium Aluminum Oxide Strips.

The sides of the fuel outlet manifold, however, were almost completely sealed. A small gap was observed on both sides next to the stack. Figure 5-30 shows a photograph of the fuel outlet manifold after firing. The side was sealed with K-glass and zirconia felt, and the top edge was sealed with S-glass and magnesium aluminum oxide strips.

5.4 LIFE TESTING

During the project long duration tests were performed on cells and stacks. These tests, each spanning several hundred hours, showed little performance degradation in cells and stacks which performed well initially. In fact, in some cases an improvement in the ASR of the stacks was observed.

Life tests were conducted on two cells (SC1351 and SC1353) during April 1991. These cells were A/E/CE trilayers with a thickness ratio of 2:1:1. The OCV of cell SC1351 was tested for 100 hr as a function of hydrogen flow rate and temperature. A plot of the OCV as a function of time is presented in Figure 5-31. Initially, the OCV decayed until the temperature was raised to 1000°C, at which time the OCV increased to 1.05 v and held steady. The OCV decreased when the fuel flow rate was decreased from 10.5 to 1 ccm and held constant at about 0.92 v for approximately 60 hr. At this point, the current density was increased from 0 to 100 ma/cm². As shown in Figure 5-32, the voltage output increased to 0.998 v and held essentially constant for

Figure 5-30. Photograph of the Fuel Outlet Manifold After Firing. The Side Was Sealed with K-glass and Zirconia Felt, and the Top Edge Was Sealed with S-glass and Magnesium Aluminum Oxide Strips.

60 hr. A 250-ma/cm^2 current density was applied to the cell for 20 hr and the voltage dropped off to 0.887 v. After 20 hr of testing, the test was ended.

Cell SC1353 (A/E/CE trilayers with a thickness ratio of 2:1:1) was life tested in June 1991 for 190 hr. See Figure 5-33. The OCV of this cell was 1.05 v. Upon increasing the current density from 0 to 100 ma/cm^2 , the cell voltage dropped off to 0.96 v; however, the cell output increased slightly to 0.98 v over the next 50 hr. When a 250 ma/cm^2 load was applied to the cell, the voltage decreased to 0.88 v and held steady for the next 140 hr until the cell fractured.

Life testing was conducted on a single cell (ED040-31) with an A:E:CE thickness ratio of 2:1:1. The cell was tested with an applied load of 250 mA/cm^2 for over 300 hr without failure. The cell voltage was 0.82 v and showed no degradation over the entire test period. The area-specific resistance or resistivity of the cell initially was 0.8 ohm-cm^2 and showed only a small change with time under load. The test was terminated after 310 hr under load. Upon cooling, the cell was examined by visual observation and optical microscopy. No unusual features were observed.

A single cell (ED065-7) was tested, containing baseline A, baseline E, and alumina-modified CE. The test was carried at 1000°C with 97 percent H_2 /3 percent H_2O fuel and air.

The cell was operated under 250 mA/cm^2 load for about 170 hours. The operation was inadvertently terminated due to brief power loss in the laboratory test

Figure 5-31. Open Circuit Voltage (OCV) as a Function of Time for Single Cell SC1351 at 1000°C

Figure 5-32. Lifetime Performance for Single Cell SC1351 at 1000°C Under Load with Air as Oxidant and H₂ as Fuel

LIFE TEST CELL 1353A
A/E/Ce; 211

Figure 5-33. Lifetime Performance of Single Cell SC1353 at 1000°C Under Load with Air as Oxidant and H₂ as Fuel

area. The initial cell voltage under the load was 0.69 V and the final cell voltage was 0.53 V. During the load operation period, the OCV decreased about 60 mV. After testing, visual examination of the cell showed debonding or dewetting of the seal material on the cathode surface. This might allow small gas cross leakage in the cell, causing performance degradation during the life test.

Single-cell stack EB023-02 was held under an endurance test for nearly 200 hr. Open-circuit voltage and area-specific resistance were checked on a regular basis. Performance for the stack is shown in Figure 5-34. As can be seen, OCV's were relatively stable, while ASR gradually increased (higher resistances) over a period of days ranging from 1.7 to 2.4 ohm-cm², with the exception of the first day under test. It is not fully understood why the initial curve for day 1 is lower than the following days. It is speculated that the nickel in the anode was still being reduced, but this would be difficult to verify at operating conditions. The curves generated for Figure 5-34 were all taken with 20 percent H₂/80 percent He (humidified), and air at 1000°C. Stack EB023-02 was tested with a variety of fuel concentrations and humidities, to determine their effect on performance. By running the stack without humidity, and 20 percent H₂/80 percent He, an OCV of 0.965 was obtained.

A life test was performed on two-cell stack EE344-03 using a glass sealant for manifolding. Stack EE344-03 was tested with an applied load of 200 ma for approximately 600 hr. The initial stack voltage at a 200-ma load was 1.28 v. The stack voltage showed an improvement to 1.43 v over time. The ASR of the stack initially was 2.5 ohm-cm². After 600 hr of operation, the ASR of stack EE344-03 improved to 2.15 ohm-cm².

5.5 PARAMETRIC STUDIES

A two-cell stack was tested on simulated coal gas (67 percent hydrogen, 22 percent carbon monoxide, 11 percent water) and air at 800°C, 900°C, 1000°C, and 1050°C. The results of the tests are shown in Figure 5-35. A two-cell stack was tested in humidified hydrogen and air at 800°C, 900°C, 1000°C, and 1050°C. The results of these tests are shown in Figure 5-36.

5.6 POSTTEST ANALYSIS

A posttest analysis of stacks was undertaken to examine fuel cell stacks after operation. Fuel cell stacks designated for examination are first vacuum-impregnated with epoxy. Then the specimens are sectioned and polished. The sectioned specimens are then microscopically evaluated and the defects are categorized by type, location, and number per unit length or area. See Table 5-7.

Reviewed below are the analyses of most of the tested stacks which failed to meet performance goals.

- Stack ST1085: Single-cell stack ST1085 showed a high area-specific resistance (52.8 Ω-cm²). The corrugated anode remained well joined to both the electrolyte and the anode flat plate. This anode was received in the oxidized

Figure 5-34. Performance of ASE MSOFC Single-Cell Stack EB023-02

IG-14281

Figure 5-35. Two-Cell Stack Performance with 67% H₂ + 22% CO + 11% H₂O/Air

IG-14282

Figure 5-36. Two-Cell Stack Performance with 97% H₂ + 3% H₂O/Air

TABLE 5-7		
RESULTS OF POSTTEST ANALYSIS		
Stack	Overall Length of Cell Section, cm	No. of Fractures Through Electrolyte Thickness
ST1085 (one electrolyte)	4.4	8
	4.4	12
	3.9	8
	3.1	6
	2.9	5
ST1084 (one electrolyte)	3.2	8
	3.1	11
	2.8	9
	2.7	8
	2.7	7

condition, whereas, if a cell is terminated under reducing conditions, analysis can be made regarding the effect of electrolyte fractures by the amount of metallic nickel present near the crack. The cathode corrugations remain joined to the cathode flat plate, but were separated from the electrolyte at all locations.

- Stack ST1084: Cell ST1084 appeared to have been terminated with hydrogen present with the anode, as evidenced by the presence of metallic nickel. Every electrolyte/anode corrugation in the five sections of cell examined was separated. Typically, the separation consisted of one-third of the electrolyte thickness being torn away. The corrugated cathode remained joined to the electrolyte but had occasional separation from the flat layer.
- Stack EG259-02: This stack was a two-cell stack fabricated by bonding two electrode-covered modules to an interconnect. The stack had some minor cracks in the anode and cathode layers. Most of these cracks may have resulted from the mounting and sectioning process. The CE/I bonds appear good, with a large number of contact points between the corrugations and the interconnect layer. The A/I bonds show cracking and separation away from both the anode corrugations and the interconnect flat plate. However, this may just be in the areas observed since this stack showed reasonable performance.

The major defect observed in the stack is that the well through which the current collector exits the manifold was not sealed on the anode side of the stack. In fact, two thirds of the length of the stack were exposed to air, which allowed the fuel to leak from the stack during testing. It is believed that the major part of the performance losses of this stack during testing is due to the incomplete seal around the current collector on the anode side of the stack.

- Stack EH15-1: This was a two-cell stack fabricated by bonding two single-cell stacks together with an interconnect. The anode of the stack was observed to be partially oxidized during cooling. This allowed cracks in the anode prior to sectioning to be discriminated from those resulting from manifolding or processing. There were several cracks observed in the anode corrugates. Cracks were also observed in the A/E/CE trilayer. These cracks could be caused by mounting or cutting the stack.

The stack was sectioned perpendicular to the anode and cathode corrugates and at 45° to the corrugates. In all cross sections, the bond materials did not make complete contact to provide a pathway for current flow. The poor performance of this two-cell stack appeared to be due to the poor bonding of the individual stack to the interconnect. The exact cause for this poor bonding cannot be determined from this posttest analysis. Possible causes include cycling of the stack during current collector application and manifolding.

- Stack EE316-01—The stack was a two-cell stack made by bonding two single-cell modules. The stack was manifolded with Alfrax (Carborundum Co.), an alumina based cement, instead of the zirconia based Aremco 516 currently in use. The objective of this posttest analysis was to determine possible causes for the poor performance of this stack.

No cracks could be seen on the external surfaces of the manifold or in the cement. Upon sectioning the manifolded stack, some air bubbles (pockets) were observed in the cement. The number of air pockets was much less than normally observed when the Aremco 516 is used. The cement appeared to bond well to the stack and seal off the current collectors from the air.

The stack was sectioned perpendicular to the anode and cathode cover plates and at 45 deg to the corrugates. In all sections, the bond between the intermediate corrugates and the cover plate made good contact. The anode bond, however, only made contact between the anode corrugates and the cover plate at about 30 to 40 percent of the bond sites observed. The bonds toward the edge of the cell did not appear to make any contact between the cover plate and the corrugations. The delamination or fracture of the anode bond material occurred near the anode cover plate. The anode corrugates also showed distortion from their sinusoidal shape to a square

wave shape. This distortion can be related to the processing of the tape and the constraint weight used during sintering.

From this posttest analysis, the reasons for the poor performance of this stack cannot be determined.

- Stack EE309-02—The stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. The stack was manifolded with the Aremco 516 cement.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. In all sections observed the bond between the intermediate corrugates and the cover plate made good contact.

The anode bond made contact between the anode corrugates and the cover plate in about 30 to 40 percent of the bond sites. The bond material at the bond site was relatively thick and contained some very large cracks. The delamination or fracture occurred near the anode cover plate. There were some cracks observed in the anode and cathode corrugation and cover plates and in the trilayer, but not severe enough to prevent the stack from operating.

The analysis did not identify any cracking or delamination that could explain the poor performance of this stack. The reasons for the observed performance of the stack cannot be determined from this posttest analysis.

- Stack EE305-01—Stack EE305-01 was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. Aremco 516 cement was used in manifold sealing.

The anode corrugates showed good bonding to the anode cover plate. As noted in the previous posttest analysis, the anode bond was relatively thick and had some air pockets and cracks in it. There were some cracks in the anode corrugates and cover plate.

The A/E/CE trilayer showed several significant cracks in the trilayer region. Larger cracks filled with epoxy were observed in all cross sections, indicating that the cracks existed before the stack was mounted.

The CE corrugation bonded with the interconnect cover plate except near the edges of the cell. The last three to four corrugates near the edge did not bond with the cover plate. The bond material appeared to be pulled away from the corrugation. There were some cracks observed in both the interconnect flat plate and the cathode corrugations.

It appears that the poor performance of this stack was due to the cracks in the A/E/CE trilayer. The number and degree of these cracks were more severe than in the last several stack tests.

- Stack EE332-01—This stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. This stack was manifolded with Aremco 516 cement.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. The bond between the intermediate corrugates and the cover plate appeared to make good contact and was intact in all sections observed.

The anode bond made good contact between the anode corrugates and the anode cover plate. Only one or two of the bonds were fractured, a significant improvement over previous stacks analyzed. The anode bond was thinner than those used in previous stacks. The delamination or fracture occurred near the anode cover plate.

There were some cracks observed in the anode and cathode corrugation and the A/E/CE trilayer; however, they were not severe.

From this analysis, the improved performance of this stack is believed to be due to the improvement of the anode bonds. The improvement of the bonds may be related to technique and the use of less (e.g., thinner tapes) material to bond the corrugations to the flat plates.

- Stack EE303-02—The stack was a single-cell stack made by bonding a single-cell module with anode and cathode cover plates. The manifold of this stack was sealed using Corning glass.

When the manifold was placed under vacuum to infiltrate the fuel cell with polymer, air was observed to leak from the manifold from the sidebars. The largest leak was observed around the fuel inlet.

The stack was sectioned perpendicular to the anode and cathode cover plates at 45 deg to the corrugates. In all sections, the bonds appeared to make good contact between the corrugates and the cover plates. Only one or two of the anode bonds were separated from the anode cover plate.

There was little damage to the stack from the new glass sealant. Some reactions between the glass and the electrodes were observed on the edge of the stack. In the case of the anode where the glass was in contact with the stack, the anode did not reduce. Portions of the top cover plate, several hundred microns in length, around the edges of the stack did not reduce during the testing of this stack.

There were some cracks observed in the anode and cathode corrugation and the A/E/CE trilayer. There were several severe cracks in the A/E/CE trilayer. However, they may have occurred on cooling, resulting from the new sealing material. The new glass sealing material did not seal the manifold completely. This may be overcome by applying more glass to the manifold. The glass appeared to be relatively inert, having little effect on the fuel cell and did not appear to lead to any unusual damage upon cooling.

6. PERFORMANCE AND COST ANALYSIS

In this task a detailed electrochemical performance model of an MSOFC called FCELL, originally developed at ANL, was modified by ASE and ANL to incorporate more accurate and comprehensive thermal and chemical analyses. This model was then used to evaluate stack performance as a function of fuel type and stack operating conditions. Finally, the stack model was coupled with a system simulation model capable of modeling mass and energy balances in chemical process equipment to perform system configuration studies. These studies projected very high efficiencies for a 2-Mw natural-gas-fired plant based on MSOFC technology.

Additionally, the stack manufacturing costs previously developed under DOE/METC Contract DE-AC21-88MC25166, "Yttria-stabilized Zirconia Solid Oxide Electrolyte Fuel Cells-Monolithic Solid Oxide Fuel Cells," were updated with information gained from material suppliers and to reflect the change in the MSOFC technology base associated with the incorporation of thin-film electrolytes.

Finally, an assessment of the market for distributed commercial power for the MSOFC technology was undertaken and the results are incorporated in this report.

The principal results of this task are presented in some detail in the topical report entitled "Performance and Cost Analysis of Monolithic Solid Oxide Fuel Cells," ASE Document 94-66925, published March 1994. Presented here are details of the stack performance model and market assessment with an overview of the updated costs and system optimization studies which are reviewed in the topical report.

6.1 STACK PERFORMANCE MODEL

A detailed mathematical model of a crossflow MSOFC called FCELL, originally developed by Argonne National Laboratory and significantly modified by ASE, was used in characterizing the components and power systems described in this report. FCELL simulates MSOFC operation with a variety of fuels, such as hydrogen, hydrocarbon fuels, and coal gas. The modified model considers the electrochemical, electrical, chemical equilibrium, operating pressure, and pressure drop characteristics associated with these fuels, as well as realistic heat transfer characteristics and extended applicability of a variety of potent fuel reactants to the crossflow geometric MSOFC configuration.

In an MSOFC, fuel and oxidant combine electrochemically across a solid oxide electrolyte to form dc current. The MSOFC is constructed of alternating layers of anode, electrolyte, cathode, and interconnect materials. A single cell is shown schematically in Figure 6-1. In this cell, oxidant flows through passages in a porous cathode layer. The oxygen accepts electrons from an external circuit and forms oxide ions.

These ions are conducted through the electrolyte layer to the anode. Fuel flows through passages in the porous anode, and hydrogen from the fuel stream combines with the oxide ions to form water and to liberate electrons. The freed electrons are conducted through a nonporous interconnect layer that separates multiple cells in a stack. The cells are stacked in electrical series to build voltage.

Figure 6-1. Solid Oxide Fuel Cell Chemistry

Model FCELL simulates the operation of a fuel cell with a cross flow configuration (fuel and air streams perpendicular to one another). The program can model either rectangular passage geometry or triangular passage geometry, as shown in Figure 6-2. A single cell in the MSOFC stack model consists of an interconnect layer with a thin layer of anode and cathode material on either side, an electrolyte layer with a thin layer of anode and cathode material on either side, an anode flow passage, and a cathode flow passage. These eight layers are shown in Figure 6-2.

(a) Rectangular Passage Geometry (b) Triangular Passage Geometry

Figure 6-2. Cross Flow MSOFC Passage Geometry

FCELL simulates the performance of a MSOFC stack by calculating the performance of a single cell within the stack. The model assumes that all the cells have the same performance of a single cell within the stack, and thus neglects end effects. The horizontal plane of the cell is divided into small rectangular areas, or elements, with a single centrally located node. The elements are sufficiently small that nodal values of temperature, pressure, concentration, etc. can be used over the entire element for the calculation of local current densities and heat fluxes.

The mass balance, energy balance, chemical equilibrium, and expressions for the electrochemical and electrical phenomena are set up and solved for each element. The model can simulate hydrogen, diesel, or coal gas operation. In fact, any fuel made up of any or all of the following constituents can be modeled:

H₂, H₂O, C₁₆H₃₄ (simulated diesel fuel), CO, CO₂, CH₄, O₂, N₂

The oxidant can be any mixture of oxygen and nitrogen.

6.1.1 Electrical and Electrochemical Characteristics

The thermodynamic reversible cell voltage, or Nernst potential, at any node (*i,j*) is obtained from the following relationship:

$$E_{i,j} = E^{\circ}_{i,j} + RT_{f,avg}/nF \ln (P_{H_2,avg} P_{O_2,avg}^{0.5} / P_{H_2O,avg})$$

where $E^{\circ}_{i,j} = -\Delta G_r [T_{f,avg}]/nF$

The electrical resistance at each node is calculated from the resistivities of the individual layers (electrolyte, interconnect, anode, and cathode) and the path length of the electrons and ions. The program calculates approximate path lengths from the geometry of the cell. Constant resistivities are assumed for all layers except for the electrolyte, for which the resistivity is calculated using an expression of the form

$$A_o + B_o \exp[C/T_{e,i,j}]$$

The user may choose to estimate or calculate the resistance from some other source—for example, test data—or from a finite element analysis. These estimated or calculated resistance values may be used in the program, if desired.

Assuming a cell operating voltage of *V* volts, the current generated in the node is

$$I_{i,j} = (E_{i,j} - V) / R_{i,j}$$

6.1.2 Chemical Equilibrium and Fluid Properties

The MSOFC program determines the composition of the fuel stream by assuming that chemical equilibrium is achieved in each element. The chemical equilibrium program STANJAN, written by Professor W.C. Reynolds of Stanford University, has been incorporated into FCELL to calculate the equilibrium composition and enthalpy of the fuel stream. STANJAN uses the element-potential method for chemical equilibrium analysis. STANJAN must have access to a data file containing the thermochemical data

for the species involved in the chemical equilibrium calculations. Sources for the fluid property data used in STANJAN and FCELL are listed in Table 6-1.

6.1.3 Heat Transfer Characteristics

Two separate heat transfer algorithms are available in FCELL. A simplified heat transfer algorithm solves three energy balances to determine the electrolyte temperature and the fuel and oxidant exit temperatures for each node. This routine assumes that the heat transfer area for convection from the fluid streams to the anode or cathode layer is simply the footprint area of the element.

TABLE 6-1	
STANJAN AND FCELL FLUID PROPERTY DATA SOURCES	
Constituent	Data Source*
H ₂ O	1, 2
H ₂	1, 2
CO	1, 2
CO ₂	1, 2
CH ₄	1, 2
O ₂	1, 2
N ₂	1, 2
C ₁₆ H ₃₄	3, 4
*Data sources:	
1 = JANNAF thermochemical tables	
2 = Computer program GASPLUS, developed by Fowler, J.R. (Sverdrup Technology Inc.) and Hendricks, R.C. (NASA Lewis Research Center)	
3 = Stull, D.R., Westrum Jr., E.F. and Sinke, G.C., "Chemical Thermodynamics of Compounds"	
4 = Rossini et al, "Selected Values of Properties of Hydrocarbons," NBS Circular, November 1947	

The second heat transfer algorithm contains a more detailed calculation that accounts for the fin areas in the total heat transfer area. This second algorithm also allows matrix conduction effects to be considered. The more detailed model requires more computation time, but is closer to reality.

6.1.4 Simplified Heat Transfer Characteristics

The simplified heat transfer algorithm assumes that all of the heat is released in the electrolyte layer. The air and fuel side heat transfer coefficients, h_a and h_f , are calculated on a limiting Nusselt number of 3.0. The following equations are solved to determine the unknown electrolyte temperature, T_e , at each element; fuel temperature at the outlet of each element, $T_{f,i,j}$; and oxidant temperature at the outlet of each element, $T_{a,i,j}$

- (a) Cathode energy balance:

$$W_{a,out}H_{a,out} - W_{a,in}H_{a,in} - UA(T_{f,avg} - T_{a,avg}) - h_a A(T_e - T_{a,avg}) + W_{O_2}H_{O_2} = 0$$

- (b) Anode energy balance:

$$W_{f,out}H_{f,out} - W_{f,in}H_{f,in} + UA(T_{f,avg} - T_{a,avg}) - h_f A(T_e - T_{f,avg}) + W_{H_2}H_{H_2} - W_{H_2O}H_{H_2O} = 0$$

- (c) Electrolyte energy balance:

$$h_f A(T_e - T_{f,avg}) + h_a A(T_e - T_{a,avg}) - Q_{i,j} = 0$$

$$\text{where } Q_{i,j} = (\Delta G_r[T_{f,avg}] - \Delta H_r[T_{f,avg}])I_{i,j}/nF + I_{i,j}^2 R_{i,j}$$

$$\text{and } T_{f,avg} = (T_{f,in} + T_{f,i,j})/2$$

$$T_{a,avg} = (T_{a,in} + T_{a,i,j})/2$$

6.1.5 Detailed Heat Transfer Characteristics

The second heat transfer routine calculates the temperature at each of the eight layers in the fuel cell. Traditional fin efficiency calculations cannot be used in this case because the fin is bounded by plates on either side that are at different temperatures. This algorithm uses a method published by Kraus, Snider, and Doty (the KSD method) to account for the fins or webs in the heat transfer calculation.

Eight energy balances are solved to give the eight temperatures; the energy flows and temperatures are shown schematically in Figure 6-3:

- (a) Electrolyte energy balance:

$$Q_{Me} - P_e - Q_{ox,e} - Q_{f,e} + W_{H_2}H_{H_2} + W_{O_2}H_{O_2} - W_{H_2O}H_{H_2O} = 0$$

- (b) Interconnect energy balance:

$$Q_{Mi} - Q_{ox,i} - Q_{f,i} = 0$$

- (c) Anode on interconnect energy balance:

$$Q_{f,i} - Q_{ff,i} - Q_{fpr,i} + Q_{Mai} = 0$$

- (d) Anode on electrolyte energy balance:

IG-12614-A

Figure 6-3. Energy Flows and Temperatures Calculated Using MSOFC Detailed Heat Transfer Model

$$Q_{f,e} - Q_{ff,e} - Q_{fpr,e} + Q_{Mae} = 0$$

(e) Cathode on interconnect energy balance:

$$Q_{ox,i} - Q_{oxf,i} - Q_{oxpr,i} + Q_{Mci} = 0$$

(f) Cathode on electrolyte energy balance:

$$Q_{ox,e} - Q_{oxf,e} - Q_{oxpr,e} + Q_{Mce} = 0$$

(g) Fuel energy balance:

$$Q_{ff,i} + Q_{fpr,i} + Q_{ff,e} + Q_{fpr,e} + W_{f,in}H_{f,in} - W_{f,out}H_{f,out} + W_{H_2O}H_{H_2O} - W_{H_2}H_{H_2} = 0$$

(h) Oxidant energy balance:

$$Q_{oxf,i} + Q_{oxpr,i} + Q_{oxf,e} + Q_{oxpr,e} + W_{ox,in}H_{ox,in} - W_{ox,out}H_{ox,out} - W_{O_2}H_{O_2} = 0$$

Energy terms:

P_e = Power

Q_{Me} = Matrix conduction term for electrolyte layer

Q_{Mi} = Matrix conduction term for interconnect layer

Q_{Mai} = Matrix conduction term for anode on interconnect layer

Q_{Mae} = Matrix conduction term for anode on electrolyte layer

Q_{Mci} = Matrix conduction term for cathode on interconnect layer

Q_{Mce} = Matrix conduction term for cathode on electrolyte layer

$Q_{f,e}$ = Heat flow from electrolyte to fuel stream

$Q_{ox,e}$ = Heat flow from electrolyte to oxidant stream

$Q_{f,i}$ = Heat flow from interconnect to fuel stream

$Q_{ox,i}$ = Heat flow from interconnect to oxidant stream

$Q_{ff,i}$ = Heat flow from anode on interconnect layer into fin

$Q_{fpr,i}$ = Heat flow from anode on interconnect prime surface area into fuel

$Q_{ff,e}$ = Heat flow from anode on electrolyte layer into fin

$Q_{fpr,e}$ = Heat flow from anode on electrolyte prime surface area into fuel

$Q_{oxf,e}$ = Heat flow from cathode on electrolyte layer into fin

$Q_{oxpr,e}$ = Heat flow from cathode on electrolyte prime surface area into oxidant

$Q_{oxf,i}$ = Heat flow from cathode on interconnect layer into fin

$Q_{oxpr,i}$ = Heat flow from cathode on interconnect prime surface area into oxidant

Matrix conduction is the heat that is transferred along the plane of the interconnect, electrolyte, anode, and cathode layers. This heat transfer model has an option to calculate matrix conduction by using the temperature distribution from the previous iteration to determine the amount of energy transferred into each element from the surrounding elements. Since this algorithm uses the previous temperature distribution in solving for the temperature at the current iteration, it has the tendency to become unstable if the temperature distribution changes dramatically from one iteration to the next. To provide stability in the matrix conduction calculations, only low values of thermal conductivity should be used.

Matrix conduction tends to smooth out the temperature profile; however, it has little effect on the performance parameters such as current, power, and efficiency of the fuel cell. The matrix conduction calculations significantly increase the computation time, and therefore should only be used when an accurate temperature profile is required.

This detailed heat transfer routine assumes a Nusselt number of 3.0 for rectangular passages and a Nusselt number of 2.5 for triangular passages. The heat transfer coefficients are calculated from

$$h = \text{Nu} k_{\text{th}} / (4r_h)$$

where Nu = Nusselt number

k_{th} = thermal conductivity of the fluid

r_h = hydraulic radius of the flow passage

6.1.6 Flow Distribution

FCELL has four separate options for calculating the flow distribution; in all of these options, the flow distribution is assumed to be uniform across the width of an element:

- (a) Option 1. Assumes a uniform flow distribution across the entire fluid flow width and oxidant flow width.
- (b) Option 2. Assumes a linear flow distribution across the fuel and oxidant flow widths.
- (c) Option 3. Allows the user to specify the flow fraction through each element across the fuel and oxidant flow widths. This option is useful in testing the effects of blocked passages.
- (d) Option 4. Calculates the flow distribution required to give a uniform pressure drop across the fuel cell. To accomplish this, the program guesses at a flow distribution, performs all fuel cell calculations, checks the pressure drops through the cell, readjusts the flow, and repeats the calculations. This method gives the most accurate fuel cell performance and pressure drops; however, it requires considerably more execution time.

6.1.7 Pressure Drop Calculations

The pressure drop calculations assume that fully developed laminar flow exists in the small flow channels. The pressure drop is calculated by

$$\Delta P = (W_{\mu}KL)/ab^3pg_c)$$

6.1.8 Iteration Scheme

The equations given in paras. 6.1.1 through 6.1.5 contain a combination of inlet, outlet, and average conditions. Since the outlet conditions are not known ahead of time, an iteration scheme is used. The solution starts at the node at which the fuel and air inlet edges meet, because both inlet streams are completely defined. The average partial pressures and exit temperatures of the node are assumed, and a first estimate of the Nernst potential is obtained. The resistance and current are calculated, then the heat transfer calculations are performed.

The new value for the electrolyte temperature is used to recalculate the Nernst potential and resistance. These iterations continue until the temperature change less than a specified tolerance from iteration to the next. The mass flow rates of H_2 , H_2O , and O_2 are then adjusted based on the calculated current, and the equilibrium composition of the node is calculated using STANJAN. The pressure drop through the node is calculated. The partial pressures of the constituents are recalculated and compared to the previous value. The entire iteration scheme is repeated until convergence on the partial pressures has been reached.

6.1.9 User Inputs

FCELL can operate as a stand-alone program or can be incorporated into a system model using the steady-state system modeling tool MECANO, developed by K.P. Barr of ASE. The inputs to FCELL are saved in a data file. If the model is used as a stand-alone program, the user inputs can be entered or modified interactively by a menu-driven routine. If the model is incorporated into a system program, the user inputs must be entered and modified through a data file.

The user specifies the geometry of the fuel cell, the materials data, the process data, and the program controls. Summaries of user geometric, materials, and process input data are given in Tables 6-2, 6-3, and 6-4 respectively.

The geometric input data (Table 6-2) allows the user to specify the detailed geometry of the fuel cell. FCELL can perform calculations for a fuel cell with rectangular passage geometry or triangular passage geometry.

The materials input data (Table 6-3) describe the material properties for the ceramics that make up the fuel cell.

TABLE 6-2	
GEOMETRIC INPUT DATA	
Item	Description
IGEOM	Geometry indicator 0 = Rectangular channels 1 = Triangular channels
N	Number of nodes in oxidant flow length
M	Number of nodes in fuel flow length
NCELL	Number of cells in stack
TE	Electrolyte layer thickness, cm
TI	Interconnect layer thickness, cm
TAE	Thickness of anode layer on electrolyte, cm
TCE	Thickness of cathode layer on electrolyte, cm
TAI	Thickness of anode layer on interconnect, cm
TCI	Thickness of cathode layer on interconnect, cm
WA	Thickness of anode web (fin), cm
HA	Height of anode passage, cm
XA	Anode web (fin) spacing, cm For rectangular fins, fin spacing is the gap between fins (not counting fin thickness). For triangular fins, fin spacing is the distance from peak to peak.
WC	Thickness of cathode web (fin), cm
HC	Height of cathode passage, cm
XC	Cathode web (fin) spacing, cm For rectangular fins, fin spacing is the gap between fins (not counting fin thickness). For triangular fins, fin spacing is the distance from peak to peak.
XN	Length of fuel inlet edge, cm
XM	Length of oxidant inlet edge, cm

TABLE 6-3	
MATERIALS INPUT DATA	
Item	Description
RAIF	Anode interfacial resistance, ohm-cm ²
RCIF	Cathode interfacial resistance, ohm-cm ²
IRI	Interconnect and corrugate resistance specification 1 = Specify resistivity of layers and calculate resistance based on geometry 2 = Specify area-specific resistance (ASR) of interconnect and adjacent corrugated layers
ASRI	If IRI = 2, specify ASR of interconnect and adjacent corrugated layers, ohm-cm ²
RHOA	Anode material resistivity, ohm-cm ²
RHOC	Cathode material resistivity, ohm-cm
RHOI	Interconnect material resistivity, ohm-cm
AA	Electrolyte resistivity calculated from $RHOE = AA + BB * \exp(CC/T)$
BB	(Same as for item AA)
CC	(Same as for item AA)
DENSE	Density of electrolyte layer
DENSA	Density of anode layer
DENSC	Density of cathode layer
DENSI	Density of interconnect layer

The process data (Table 6-4) are the input conditions to the fuel cell. For a straight-through calculation (one pass through the program), the user must specify the inlet fuel and oxidant flow rates and the stack voltage. From these, FCELL calculates, among other values, the cell current, the maximum cell temperature, and the fuel utilization. If a specific cell current, maximum cell temperature, or fuel utilization is desired, it can be used as an input parameter. FCELL employs a Newton-Raphson iteration to vary the inlet flow rates or cell voltage a number of times to achieve the desired current, cell temperature, or fuel utilization.

TABLE 6-4
PROCESS INPUT DATA

Item	Description
IX()	An array to specify which three of the following will be input parameters (the remaining three will be calculated by the program): IX(n) = 1: Air inlet flow rate is input IX(n) = 2: Fuel inlet flow rate is input IX(n) = 3: Stack voltage is input IX(n) = 4: Current is input IX(n) = 5: Maximum cell temperature is input IX(n) = 6: Fuel utilization is input
VIX()	IX(n) = 1: VIX(1) = air inlet flow, standard L/hr; otherwise, VIX(1) = initial guess at air inlet flow IX(n) = 2: VIX(2) = fuel inlet flow, standard L/hr; otherwise, VIX(2) = initial guess at fuel inlet flow IX(n) = 3: VIX(3) = stack voltage, v; otherwise, VIX(3) = initial guess at stack voltage IX(n) = 4: VIX(4) = current amps; otherwise, VIX(4) = not used IX(n) = 5: VIX(5) = maximum cell temperature, K; otherwise, VIX(5) = not used IX(n) = 6: VIX(6) = fuel utilization; otherwise, VIX(6) = not used
ZFIN()	Mole fractions of constituents in the inlet fuel stream: ZFIN(1) = fraction of $C_{16}H_{34}$ ZFIN(2) = fraction of H_2 ZFIN(3) = fraction of H_2O ZFIN(4) = fraction of CO ZFIN(5) = fraction of CO_2 ZFIN(6) = fraction of CH_4 ZFIN(7) = fraction of O_2 ZFIN(8) = fraction of N_2
XO2IN	Mole fraction of O_2 in inlet oxidant stream (balance assumed to be N_2)
TFUEL	Inlet fuel temperature, K
TAIR	Inlet oxidant temperature, K
PFUEL	Inlet fuel pressure, atm
PAIR	Inlet oxidant pressure, atm

6.1.10 FCELL Program Output

A typical sample printout of the computer output from FCELL is presented as Figure 6-4, which echoes the program input geometric, materials, and process data. Figures 6-5 through 6-9 are three-dimensional plots of the nodal values of electrolyte temperature, current density, Nernst potential, oxygen pressure, and hydrogen pressure throughout the fuel cell. These plots were generated by the software package MathCad from matrixes of numbers generated by FCELL. In this model, the fuel stream flows from the left to the right of the cell, and the air stream flows from the bottom to the top.

6.1.11 Results

To illustrate the types of results obtainable with the model, some test cases were run with a fuel gas consisting of 97% H_2 -3% H_2O as the anode gas. The input parameters for a base case are given in Table 6-5. The cell operation is simulated subject to conditions of 85 percent fuel utilization and a maximum cell temperature of 1050°C. The simulation algorithm uses an initial value rather than a boundary value approach for the solution of the appropriate differential equations. Therefore, these two conditions of fuel utilization and maximum cell temperature are satisfied by successively iterating over the fuel and air flow rates, keeping the rest of the input parameters constant.

The calculated results are summarized in Table 6-6. Under these conditions, the cell layer generates 17.5 w of power at an average current density of 289 mA/cm² and a fuel conversion efficiency of 49 percent. The pressure drop calculations show that the air and fuel blowers will consume energy equivalent to 5.8 percent of the gross electrical power produced by the cell for a net power production of 16.5 w.

The air stream, in addition to providing the oxidant, also serves to remove the excess heat generated in the fuel cell stack. Because of the limitation on the maximum cell temperature, the required air flow rate is relatively high, resulting in a low oxidant utilization rate. If the maximum permissible cell temperature can be increased above the 1050°C used in the base case above, the required air flow rate would be reduced, leading to a lower power consumption by the blowers and an increase in the net power production by the fuel cell.

6.1.11.1 Temperature Profile Across the Cell

Figure 6-10 shows the computed temperature distribution across the cell layer. The sharpest temperature gradients exist in the direction of fuel flow. The maximum temperature is found close to the fuel inlet edge at the air outlet edge. This region operates at higher temperatures because (a) the air entering these nodes does so at higher temperatures, as it contains sensible heat picked up from previous nodes; and (b) the combination of high Nernst potential (hydrogen rich fuel stream) and lower cell resistance (cell resistance decreases as cell temperature increases) result in high current densities and heat generation. A temperature profile across the cell is important for locating and quantifying the magnitude of the hot spots. It also shows the temperature

Run case:

```
GEOMETRIC INPUT DATA                                     cm
Number of nodes in oxidant flow length                   10
Number of nodes in fuel flow length                     10
Number cells in stack                                   1
Fuel cell has triangular channels
Electrolyte thickness, cm                               0.0064
Anode thickness on electrolyte, cm                      0.0127
Cathode thickness on electrolyte, cm                    0.0064
Interconnect thickness, cm                              0.0254
Anode thickness on interconnect, cm                     0.0127
Cathode thickness on interconnect, cm                   0.0064
Anode web thickness, cm                                 0.0254
Cathode web thickness, cm                               0.0254
Anode web height, cm                                    0.13
Cathode web height, cm                                  0.13
Anode web spacing, cm                                   0.25
Cathode web spacing, cm                                 0.25
Fuel edge length, cm                                    12.60
Oxidant edge length, cm                                 17.80

MATERIALS INPUT DATA
Anode resistivity, ohm-cm                               0.1400E-02
Cathode resistivity, ohm-cm                             0.1860E-01
Interconnect resistivity, ohm-cm                       0.5000E+00
Electrolyte resistivity, ohm-cm
    0.3680E+00 + 0.2840E-02 EXP( 10300.0/T)
Anode interfacial resistance, ohm-cm2                   0.1000E+00
Cathode interfacial resistance, ohm-cm2                 0.1000E+00
Anode bulk density, g/cm3                               4.460
Cathode bulk density, g/cm3                             4.930
Electrolyte bulk density, g/cm3                         5.710
Interconnect bulk density, g/cm3                       6.320
Electrolyte thermal conductivity, W/cm-K                0.0200
Interconnect thermal conductivity, W/cm-K               0.0200
Anode thermal conductivity, W/cm-K                     0.0200
Cathode thermal conductivity, W/cm-K                   0.0200

PROCESS DATA
Vol. fractions in fuel inlet :
C16H34 = 0.000000   H2 = 0.580397   H2O = 0.183398
CO      = 0.121373   CO2 = 0.108017   CH4 = 0.006815
O2      = 0.000000   N2 = 0.000000
Fuel inlet temperature, C                               726.85
Fuel inlet pressure, atm                                 1.224
Fuel inlet flow, Std L/h, (gm/s)                        139.11 ( 0.2198E-01)
Vol. fraction O2 in oxidant inlet                       0.210
Air inlet temperature, C                                726.85
Air inlet pressure, atm                                  1.224
Air inlet flow, Std L/h, (gm/s)                         1534.08 ( 0.5489E+00)
Cell operating voltage, V                               0.5000
Stack operating voltage, V                              0.50

PROGRAM CONTROL DATA
KSD heat transfer calculations performed

OUTPUT DATA SUMMARY
Fuel utilization, percent                               86.276
Oxygen utilization percent                               13.755
```

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Figure 6-4. FCELL Program Sample Output

Overall fuel efficiency, percent	44.920
Total cell power, Watts	106.24
Total cell current, Amp	212.475
Volume power density, kW/L	1.463
Weight power density, kW/kg	0.665
Air side pressure drop, atm	0.001906
Fuel side pressure drop, atm	0.000139
Cell bulk density, g/cm ³	2.199
Overall Energy Balance, %	0.115
Overall Mass Balance, %	0.000
Cell Area Specific Resistance, ohm-cm ²	0.42621
Average air outlet temperature, C	987.41
Average fuel outlet temperature, C	841.71
Mixed air outlet temperature, C	987.53
Mixed fuel outlet temperature, C	841.91
Waste heat out as unused H ₂ , W	32.458
Average Nernst cell potential, V	0.8878
Min Temperature, C = 726.85	at I= 1 & J= 1
Max Temperature, C = 1067.03	at I=11 & J= 4 in layer E
Min Nernst Pot., V = 0.7194	at I=11 & J=11
Max Nernst Pot., V = 0.9964	at I= 2 & J= 2

Uniform Flow Distribution

B-24762

Figure 6-4. (Continued)

B-25028-A

Figure 6-5. Electrolyte Temperature Distribution

B-25029-A

Figure 6-6. Current Density Distribution

B-24491 -A

Figure 6-7. Nernst Potential

B-24492 -A

Figure 6-8. Oxygen Pressure

B-24490 -A

Figure 6-9. Hydrogen Pressure

gradients across the cell layer; these gradients result in thermal stresses in the layer which may need to be limited to acceptably low values for long operating life of the cell. Since electrolyte resistivity is temperature sensitive, the temperature distribution can also be used to obtain some idea about the cell resistance at different locations across the cell.

6.1.11.2 Current Density Distribution Across the Cell

The computed current density distribution in Figure 6-11 shows that it is highest near the intersection of the fuel inlet and air outlet edges, where both temperature and hydrogen concentration are high. The current density tapers off rapidly in the direction of the fuel flow as the hydrogen gets depleted from the fuel stream. The lowest current density is found at the intersection of the fuel outlet and air inlet edges where both temperature and hydrogen concentrations are low. The current density distribution shown in Figure 6-11 identifies the more productive and the less productive areas of the cell layer. For optimum utilization of the fuel cell, it is important to make this current density distribution as uniform as possible. Model calculations such as these can be used to investigate design and operational parameters that can help to make the current density distribution more or less uniform.

B-21718

Figure 6-10. Temperature Distribution Across the Cell Layer for the Base Case Scenario

TABLE 6-5
INPUT DATA FOR THE BASE CASE

GEOMETRIC INPUT DATA	
Electrolyte thicknesses (T_e), mm	0.180
Sheet thicknesses on electrolyte (T_{ae} , T_{ce}), mm	0.025
Interconnect thickness (T_i), mm	0.120
Sheet thicknesses on interconnect (T_{ai} , T_{ci}), mm	0.025
Web thicknesses (W_a , W_c), mm	0.150
Web heights (H_a , H_c), mm	1.000
Web spacings (X_a , X_c), mm	1.000
Fuel edge length (X_M), mm	90.000
Oxidant edge length (X_N), mm	90.000
MATERIALS INPUT DATA	
Anode resistivity, ohm-cm	0.0014
Cathode resistivity, ohm-cm	0.0186
Interconnect resistivity, ohm-cm	0.5000
Electrolyte resistivity, ohm-cm	
$0.3685 + 0.002838 \exp(10300/T)$	
Anode interfacial resistance, ohm-cm ²	0.10
Cathode interfacial resistance, ohm-cm ²	0.10
Anode bulk density, g/cm ³	4.46
Cathode bulk density, g/cm ³	4.93
Electrolyte bulk density, g/cm ³	5.71
Interconnect bulk density, g/cm ³	6.32
PROCESS INPUT DATA	
Volume fraction H ₂ in fuel inlet	0.97
Fuel inlet temperature, °C	900
Fuel inlet pressure, atm	1.0
Fuel inlet flow, Std L/h	11.8
Volume fraction O ₂ in oxidant inlet	0.21
Air inlet temperature, °C	900
Air inlet pressure, atm	1.0
Air inlet flow, Std L/h	528
Cell operating voltage, v	0.75

TABLE 6-6
SUMMARY OF OUTPUT DATA FOR THE BASE CASE

Fuel utilization, percent	85.0
Oxygen utilization, percent	4.4
Overall fuel efficiency, percent	49.5
Total cell power, w	17.5
% Power to blowers, w	5.8
Net power, w	16.5
Average current density, mA/cm ²	289
Average cell temperature, °C	928
Average Nernst potential, v	0.89
Weight power density, kw/kg	0.62
Maximum cell temperature, °C	1050
Maximum temperature gradient, °C/cm	249

6.1.11.3 Gross and Net Power Production

The cell operating voltage strongly influences the power production and general performance of the SOFC. Figure 6-12 shows the effect of the operating voltage on the gross and net powers obtainable from the cell layer. The figure shows the existence of distinct optimum operating voltages at which the power (gross or net) can be maximized. At high cell voltages, the gross power increases with decreasing voltage, rising from 10 w at 0.8 v to a maximum of 37 w at 0.42 v. With further reductions in cell voltage, however, the increase in cell current does not make up for the decrease in cell voltage, resulting in a lower power generation. Similarly, the net power (gross power minus the power consumed by the air blower) increases with decreasing cell voltage at high cell voltages to a maximum of 31 w at 0.5 v, falling off sharply at lower voltages as the power consumption by the air blower rises rapidly.

6.1.11.4 Aspect Ratio

The high air side pumping energy requirement suggests that increasing the cross-sectional area for the air stream should improve the net power produced by a cell with the same active area. This can be achieved by changing the aspect ratio of the cell, more specifically, by increasing the length of the air inlet edge and proportionately reducing the fuel inlet edge. The computed performance of such a rectangular cell of area equal to that of the square cell considered heretofore is compared in Table 6-7. At the same voltage of 0.5 v for the two cells, the air blower power consumption is 13.3 percent of the gross power in the rectangular cell, compared with 30 percent in the square cell. The rectangular cell thus provides an increase of almost 24 percent in net power over the net power produced by the square cell. Table 6-7 also shows that all of the other cell performance parameters are essentially the same for the two cells.

Figure 6-12 shows a plot of the gross and the net power for the square and the rectangular cell as a function of cell voltage. It is evident that the rectangular cell performs better in terms of deliverable electrical power and this advantage becomes more prominent as the cell voltage decreases, an operational regime of high current densities and high heat generation, in which high air flow rates are needed.

The model calculations summarized in Table 6-7 show another significant advantage of the rectangular cell over the square cell. The maximum temperature gradient in the rectangular cell is only 67 percent of that in the square cell, leading to lower thermal stresses in the former compared to those in the latter.

B-21719

Figure 6-11. Current Density Distribution Across the Cell Layer for the Base Case Scenario

Figure 6-12. Power Generated by a Square (9 by 9 cm) Cell and a Rectangular (13.5 by 6 cm) Cell as a function of the Operating Voltage. (Fuel Utilization = 85%, T_{max} = 1050°C)

TABLE 6-7

PERFORMANCE COMPARISON BETWEEN SQUARE AND RECTANGULAR CELLS

Performance Parameters	Cells	
	Square	Rectangular
Air inlet edge, cm	9.0	13.5
Fuel inlet edge, cm	9.0	6.0
Total cell area, cm ²	81	81
Fuel flow rate, Std L/h	36	36
Air flow rate, Std L/h	1698	1698
Cell voltage, v	0.5	0.5
Fuel utilization, %	85	85
Current density, mA/cm ²	875	875
Gross power, w	35.4	35.4
% Power to blowers	30.1	13.3
Net power, w	24.8	30.7
Maximum temperature, °C	1050	1050
Maximum temperature gradient, °C/cm	249	166

6.1.11.5 Effect of Interfacial Resistance

Considerable effort is being devoted to reduce or eliminate the interfacial resistances between the anode and electrolyte and between the electrolyte and the cathode. The model can be used to assess the effects of such improvements as shown in Figure 6-13. The base case used interfacial resistance values of $0.1 \Omega\text{-cm}^2$. If the interfacial resistance can be reduced to half as much, the gross power can be increased substantially, as shown in Figure 6-13, with the improvement being most significant at the lower voltages. On the other hand, if interfacial resistances deteriorate with continued cell operation to twice those used in the base case, the gross power decreases significantly, from a maximum of 37 w at 0.42 v for the base case to a maximum of only 25 w at 0.4 v.

The base case and related results presented above are only illustrations of the types of studies that the model can be used for. More specific simulations can be run as desired. At present, however, the effort is focused mostly on enhancing and refining the model itself, rather than using the model for design or operational analyses.

B-21721

Figure 6-13. Effect of the Interfacial Resistance on the Gross Power vs Cell Voltage

6.2 MARKET ASSESSMENT AND SYSTEM CONFIGURATION STUDIES

A preliminary market assessment has been performed focusing on the markets for baseload and distributed commercial power generation. Additionally, a study of natural gas-fired plants operating at a net output power of 2 Mw has been undertaken. These studies are discussed below.

6.2.1 Assessment of MSOFC Commercial Power Market

6.2.1.1 Solid Oxide Fuel Cells-U.S. Market Forecasts

6.2.1.1.1 Methodology

6.2.1.1.1.1 Background

The impending changes driven by deregulation of the electric utility industry will give rise to the decoupling of the generation, transmission, and distribution system in the U.S. and significant growth in distributed generation. Therefore, forecasting the size and penetration rates of a new technology, namely fuel cells, is particularly challenging. The most accurate way of determining these data will eventually be achieved by undertaking detailed micro-economic studies. Such studies are difficult to undertake at present, since consistent economic analyses are still being worked out by EPRI and the utility industry.

However, based on available data from the U.S. DOE Energy Information Administration (EIA), from ASE's understanding of the drivers behind distributed generation (DG), and from the EPRI economic data on fuel cells, it is possible to build a fuel cell forecast range using reasonable boundary conditions. There are many unknowns, but the growth rate and size of the market can be broadly scaled.

6.2.1.1.1.2 Forecasting Steps

Step 1 — EIA forecasts of the additions to the U.S. electricity generation capacity are used through the year 2010. The same growth rates are used from 2011 to 2020. Three scenarios are employed: reference case (2 percent per year U.S. annual economic growth rate), best case (2.4 percent per year), and worst case (1.6 percent per year).

Step 2 — The distributed generation (DG) penetration assumption limits the DG market share of the total generation requirements to 35 percent. This is based on the EIA forecast that 39 percent of electricity production will be based on natural gas and diesel from 2001 through 2010, and most DG technologies will use these fuels. Forty-six percent will be coal-based. See Table 6-8.

Whatever the exact fuel mix will be, coal still represents the most secure and cheapest primary fuel for the U.S. The DOE clean coal initiatives focus on low emissions and high conversion efficiency technologies. The ultimate in both will be a form of pressurized fluidized bed combustor, employing hot gas filtration and a bottoming cycle

TABLE 6-8				
ADDITIONAL GENERATING CAPACITIES BY FUEL TYPE PERCENT				
	GW (1990/2000)	%	GW (2001/2010)	%
Coal/other steam	14.9	17	49.6	46
Natural gas/diesel	46.3	53	41.6	39
Oil	2.7	3	0.3	0
Nuclear	3.5	4	3.1	3
Renewable/other	20.7	23	12.4	12
Total	88.1	100	107	100

cycle using a gas turbine or fuel cell. Clearly, the most efficient system would use a solid oxide fuel cell.

Step 3 — Fuel Cell Penetration Assumptions

- (a) Distributed Generation—Fuel cells are assumed to reach their maximum at a 40-percent share of the DG segment. Fuel cells will have the most cost benefits in areas that are environmentally constrained, such as California and the northeast. However, these regions are only expected to add 15 percent of new capacity between 2001 and 2010. The regions with the greatest EIA forecast increases are the south Atlantic, midwest and southwest states at 60 percent. Because these areas are less environmentally constrained, other DG technologies, such as gas turbines and diesels, may provide significant competition to all fuel cell technologies. (See Tables 6-9 and 6-10).
- (b) Baseload Fuel Cell Penetrations—The assumptions are that the first fuel cell units will enter the market in 2008, and that a 40-percent share will be ultimately reached. Low NOx gas turbines will provide the most significant competition.

In both market segments, the ultimate penetration rates and market shares will depend on the relative life-cycle economics.

Step 4 — SOFC Penetrations. In DG markets the ultimate penetration is assumed to be 70 percent, based on the relative competitive advantages of planar-type SOFC's for low-cost manufacture, stack life in excess of 5 years, and multifuel capability. For the baseload, the share is assumed to be 100 percent, given strong potential for SOFC cost-benefit competitive advantages for bottom cycle operations.

TABLE 6-9					
REGIONAL ANALYSIS - CAPACITY ADDITIONS - REFERENCE CASE GW					
Region	1990	2000 (cum.)	1990 to 2000	2010 (cum.)	2010 to 2001
New England	1.2	4.6	3.4	5.9	1.3
NY/NJ	0.1	10.8	10.7	13	2.2
Mid-Atlantic	0.6	9.3	8.7	19.5	10.2
South Atlantic	1.2	20.8	19.6	42.5	21.7
Midwest	2.7	12.6	9.9	38.4	25.8
Southwest	1.3	11.6	10.3	28.9	17.3
Central	0.2	6.6	6.4	14.3	7.7
North Central	0	3.5	3.5	6.4	2.9
West	0.4	10.2	9.8	23.3	13.1
Northwest	0	2.6	2.6	9.1	6.5
U.S. Total	6.3	94.2	87.9	201.4	107.2

TABLE 6-10					
REGIONAL ANALYSIS - PERCENT CAPACITY ADDITIONS - REFERENCE CASE GW					
Region	1990	2000 (cum.)	1990 to 2000	2010 (cum.)	2010 to 2001
New England	19	5	4	3	1
NY/NJ	2	11	12	6	2
Mid-Atlantic	10	10	10	10	10
South Atlantic	19	22	22	21	20
Midwest	43	13	11	19	24
Southwest	21	12	12	14	16
Central	3	7	7	7	7
North Central	0	4	4	3	3
West	6	11	11	12	12
Northwest	0	3	3	5	6
U.S. Total	100	100	100	100	100

Step 5 — Stack Value Analysis. For significant DG penetration, the installed cost must be \$1000 per kw or less. For baseload plants, a total plant installation cost at \$1,600 per kw and a stack value at \$350 per kw for a 200-Mw station were assumed.

6.2.1.1.2 Results

For distributed generation and baseload forecasts, see Tables 6-11 through 6-14.

TABLE 6-11									
DISTRIBUTED GENERATION AND BASELOAD FORECASTS									
Year	U.S. Generation Additions			DG, percent	DG, Mw	Base, percent	Base, Mw	Other, percent	Other, Mw
	Utility Annual	Non- utility Annual	Total						
2001	2.58	8.14	10.72	10	1072	89	9541	1	107
2002	2.58	8.14	10.72	15	1608	83	8898	2	214
2003	2.58	8.14	10.72	20	2144	77	8254	3	322
2004	2.58	8.14	10.72	25	2680	67	7718	3	322
2005	2.58	8.14	10.72	30	3216	62	7182	3	322
2006		10.72	10.72	35	3752	62	6646	3	322
2007		10.72	10.72	35	3752	62	6646	3	322
2008		10.72	10.72	35	3752	62	6646	3	322
2009		10.72	10.72	35	3752	62	6646	3	322
2010		10.72	10.72	35	3752	62	6646	3	322
2011		11	11	35	3850	62	6820	3	330
2012		11	11	35	3850	62	6820	3	330
2013		11	11	35	3850	62	6820	3	330
2014		11	11	35	3850	62	6820	3	330
2015		11	11	35	3850	62	6820	3	330
2016		11	11	35	3850	62	6820	3	330
2017		11	11	35	3850	62	6820	3	330
2018		11	11	35	3850	62	6820	3	330
2019		11	11	35	3850	62	6820	3	330
2020		11	11	35	3850	62	6820	3	330

TABLE 6-12

PENETRATIONS – DISTRIBUTED GENERATION AND FUEL CELL MW –
REFERENCE CASE

Year	DG, percent	DG, Mw	FC, percent	FC, Mw	Base, percent	Base, Mw	FC, percent	FC, Mw	Total FC, Mw
2001	10	1072	1	11					11
2002	15	1608	2	32					32
2003	20	2144	3	64					64
2004	25	2680	5	134					134
2005	30	3216	10	322					322
2006	35	3752	15	563					563
2007	35	3752	20	750					750
2008	35	3752	25	938	62	6646	0	0	938
2009	35	3752	30	1126	62	6646	3	166	1292
2010	35	3752	35	1313	62	6646	5	332	1646
2011	35	3850	40	1540	62	6820	8	512	2052
2012	35	3850	40	1540	62	6820	15	1023	2563
2013	35	3850	40	1540	62	6820	15	1023	2563
2014	35	3850	40	1540	62	6820	25	1705	3245
2015	35	3850	40	1540	62	6820	30	2046	3586
2016	35	3850	40	1540	62	6820	35	2387	3927
2017	35	3850	40	1540	62	6820	40	2728	4268
2018	35	3850	40	1540	62	6820	40	2728	4268
2019	35	3850	40	1540	62	6820	40	2728	4268
2020	35	3850	40	1540	62	6820	40	2728	4268

TABLE 6-13

DISTRIBUTED GENERATION SOFC MW GROWTH AND 1994 \$ VALUE

Year	DG FC, Mw	SOFC Penetration, percent	SOFC Penetration, Mw	\$, kW Installed	Total \$, MM Installed	\$, MM Stack
2001	11	0	0			
2002	32	0	0			
2003	64	5	3	1500	5	2
2004	134	15	20	1250	25	13
2005	322	30	96	1000	96	48
2006	563	45	253	1000	253	127
2007	750	55	413	1000	413	206
2008	938	60	563	1000	563	281
2009	1126	65	732	1000	732	366
2010	1313	70	919	1000	919	460
2011	1540	70	1078	1000	1078	539
2012	1540	70	1078	1000	1078	539
2013	1540	70	1078	1000	1078	539
2014	1540	70	1078	1000	1078	539
2015	1540	70	1078	1000	1078	539
2016	1540	70	1078	1000	1078	539
2017	1540	70	1078	1000	1078	539
2018	1540	70	1078	1000	1078	539
2019	1540	70	1078	1000	1078	539
2020	1540	70	1078	1000	1078	539

TABLE 6-14

DISTRIBUTED GENERATION AND BASELOAD FORECASTS

Year	BASE FC, Mw	SOFC Penetration, percent	SOFC Penetration, Mw	Plant \$, kw Const	Total \$, MM Installed	Stack \$ MM
2001	0					
2002	0					
2003	0					
2004	0					
2005	0					
2006	0					
2007	0					
2008	0					
2009	166	100	166	1600	266	58
2010	332	100	332	1600	532	116
2011	512	100	512	1600	818	179
2012	1023	100	1023	1600	1637	358
2013	1023	100	1023	1600	1637	358
2014	1705	100	1705	1600	2728	597
2015	2046	100	2046	1600	3274	716
2016	2387	100	2387	1600	3819	835
2017	2728	100	2728	1600	4365	955
2018	2728	100	2728	1600	4365	955
2019	2728	100	2728	1600	4365	955
2020	2728	100	2728	1600	4365	955

6.2.1.1.2.1 Sensitivity Analyses

6.2.1.1.2.2 Economic Growth Variance

The total market value for SOFC shows a substantial variation based on the EIA's three economic growth cases. Small differences in growth account for large variations in capacity requirements. See Table 6-15 and Figures 6-14 and 6-15.

TABLE 6-15					
ECONOMIC GROWTH VARIANCE					
Year	\$, MM Reference Case, 2%	\$, MM High Growth, 2.4%	\$, MM Low Growth, 1.6%	\$, MM Reference SOFC-DG	\$, MM Reference SOFC- Baseload
2003	3	3	2	2	
2004	13	17	8	13	
2005	48	65	30	48	
2006	127	170	80	127	
2007	206	278	130	206	
2008	281	379	177	281	
2009	424	571	267	366	58
2010	576	775	363	460	116
2011	718	979	457	539	179
2012	897	1223	571	539	358
2013	897	1223	571	539	358
2014	1136	1549	723	539	597
2015	1255	1712	799	539	716
2016	1374	1874	875	539	835
2017	1494	2037	951	539	955
2018	1494	2037	951	539	955
2019	1494	2037	951	539	955
2020	1494	2037	951	539	955

Figure 6-14. SOFC Stack Value Growth – Electric Generation

Figure 6-15. Reference Case – SOFC Stack Value, DG and Baseload

6.2.1.1.2.3 Market Entry Variances

The market entry variances are as follows:

- (a) S1 – DG market penetration of 25 percent by 2001, growing at 5 percent per year to give 35 percent by 2003. This is not relevant to SOFC, since the technology does not enter the market until 2003.
- (b) S1A – This assumes S1 DG penetration and a slightly accelerated fuel cell penetration rate in 2001. Again, this is not relevant to SOFC growth.

In both cases, the underlying assumption is that SOFC achieves its technical and economic goals, providing a strong competitive advantage over phosphoric acid and molten carbonate fuel cell technologies (see Table 6-16).

TABLE 6-16			
MARKET ENTRY VARIANCES			
Year	Reference Case		
	\$, MM Base	\$, MM S1	\$, MM S1A
2001			
2002			
2003	3	4	6
2004	13	18	18
2005	48	56	56
2006	127	127	127
2007	206	206	206
2008	281	281	281
2009	424	424	424
2010	576	576	576
2011	718	718	718
2012	897	897	897
2013	897	897	897
2014	1136	1136	1136
2015	1255	1255	1255
2016	1374	1374	1374
2017	1494	1494	1494
2018	1494	1494	1494
2019	1494	1494	1494
2020	1494	1494	1494

6.2.1.2 Solid Oxide Fuel Cells — International Market Forecasts

The fuel cell market will be global. The U.S., Europe, and Japan each has the same public-policy drivers and impacts as for the automotive industry (i.e., the key U.S. driver is environmental and that elsewhere is energy efficiency).

Given the number of advanced Japanese fuel cell programs and the need for continued energy savings in Europe (which has a population greater than that of the U.S.), the global size of the SOFC market could well be triple that of the U.S. (See Table 6-17).

TABLE 6-17				
WORLD MARKET (SOFC STACKS 1994 \$ MM)				
Year	Reference Case, U.S.	Reference Case, World	High Econ. Growth, World	Low Econ. Growth, World
2001				
2002				
2003	3	10	10	5
2004	13	38	51	24
2005	48	145	195	91
2006	127	380	511	240
2007	206	619	833	390
2008	281	844	1136	532
2009	424	1272	1712	802
2010	576	1728	2326	1090
2011	718	2154	2937	1371
2012	897	2691	3670	1713
2013	897	2691	3670	1713
2014	1136	3407	4646	2168
2015	1255	3765	5135	2396
2016	1374	4123	5623	2624
2017	1494	4481	6111	2852
2018	1494	4481	6111	2852
2019	1494	4481	6111	2852
2020	1494	4481	6111	2852

6.2.2 System Configuration Studies

Only the salient points associated with the studies are discussed here. A comprehensive description of the studies is presented in ASE Document 94-66925, as discussed above.

A preliminary design analysis has been conducted on a natural gas power plant using a solid oxide fuel cell with a potential total efficiency of 72 percent. High efficiency is achieved by using a planar or monolithic solid oxide fuel cell that has sealed fuel and oxidant inlet and outlet streams. The sealed solid oxide fuel cell design allows the unreacted hydrogen in the fuel exhaust stream to be separated by a high-temperature membrane separator and recycled into the inlet fuel stream.

A performance model of the SOFC stack was coupled with a system simulation model to describe the mass and energy inputs and outputs of each process unit in the system. A 2-Mw baseline system was designed using natural gas as the fuel and recycling the hydrogen as described above. A total system efficiency (based on the higher heating value of natural gas) of 51 percent was obtained with this baseline configuration and operating conditions.

The results of a sensitivity analysis of the airflow rate, natural gas flow rate, and reformer temperature indicated that improvements in performance may be realized. Setting the airflow rate to 225 kmol/hr (6491 kg/hr), the natural gas flow rate to 10 kmol/hr (175 kg/hr), and the reformer temperature to 750°C, the SOFC system simulation was conducted, again keeping all other inlet conditions the same as the baseline case. The results of this simulation are shown in the resulting process flow diagram, Figure 6-16.

Although far from being optimal, the new process operating conditions produce a lower fuel cell power, 1,767 kw, than the 1,937 kw of electrical power (at 4,750 v) obtained from the baseline case. However, accounting for the power production and consumption of the other process units shown in Table 6-18, the "optimized" system gives an electrical efficiency of 73 percent and a total system efficiency of 72 percent.

6.3 UPDATED ASSESSMENT OF STACK COSTS

An assessment of the costs of manufacturing monolithic solid oxide fuel cell (MSOFC) stacks, assuming a nominal production rate of 200 Mw/year was performed earlier under DOE/METC Contract DE-AC21-88MC25166, "Yttria-stabilized Zirconia Solid Oxide Electrolyte Fuel Cells—Monolithic Solid Oxide Fuel Cells." The requirement for this program is to identify "critical fabrication process modifications and other changes and their impact on the cost."

B-28410

Figure 6-16. Process Flow Diagram for the "Optimized" SOFC Power Plant

TABLE 6-18		
OPTIMIZED SOFC POWER PLANT PERFORMANCE		
Process Unit	Process Unit Name	Power, kw
Air compressor	COMP-1	$W = -92$
Natural gas compressor	COMP-2	$W = -4$
Water pump	PUMP	$W = 0$
Hydrogen compressor	COMP-3	$W = -3$
Exhaust fuel turbine	TURB-1	$W = 35$
Exhaust air turbine	TURB-2	$W = 76$
Solid oxide fuel cell	SOFC	$W = 1767$
Reformer heat duty	REFORMER	$Q = 110$
Steam generator	HX8	$Q = -279$
Fuel exhaust stream	18 (FUEL-OUT)	$m = 1585 \text{ kg/hr}, T = 91^\circ\text{C}$
Air exhaust stream	27 (AIR-OUT)	$m = 5958 \text{ kg/hr}, T = 100^\circ\text{C}$
Electrical efficiency, ϵ_e		72.7 percent
Total efficiency, ϵ_T		71.6 percent
(a) Negative W corresponds to required input power; positive Q corresponds to heat input.		
(b) 30 percent of this heat goes to producing W_{steam} .		

The stack costs reported in this document consider two new factors which have emerged since the publication of the previous report:

- (a) The performance advantages of thin-film electrolytes have been established, and new stack designs will probably incorporate this feature. Accordingly, the revised cell material requirements take this into account. This proves advantageous primarily in reducing the amount of yttria-stabilized zirconia necessary for stack production.
- (b) In performing task 3.5, "Materials Supplier Identification," suppliers were surveyed in detail regarding the costs of the materials at the quantities required to produce stacks at the nominal production rate of 200 Mw per year. This resulted in some changes from the "Economic" price reported in the previous study.

6.3.1 Assessment Method

The details of the previous assessment were reported in a document entitled *Manufacturing Costs For Monolithic Solid Oxide Fuel Cell Power Generation Systems* published by the Advanced Technology Department, Power Systems, ASEA Brown Boveri, Inc. and delivered to AlliedSignal in partial fulfillment of their subcontract on the

previous study. The assessments contained there remain unchanged, except for the modifications produced by the two issues discussed above. Both coflow and crossflow approaches are evaluated. The stacks are assembled in the green state and undergo a single thermal processing cycle.

To present effectively the implications of the results of this study, it is necessary to repeat the ground rules under which the previous study was performed. Table 6-19 presents the primary cost study parameters. Table 6-20 presents the underlying assumptions concerning the plant and facility. Table 6-21 presents the production targets for the coflow and crossflow designs.

TABLE 6-19	
LIST OF PRIMARY COST STUDY PARAMETERS	
MSOFC manufacturing capacity,	200 Mw/year
Manufacturing period,	10 years
Manufacturing unit	
Coflow,	50 kw stack
Crossflow,	25 kw stack
Power density	
Voltage,	0.85 vdc
Current,	300 ma/sq cm
Tape fabrication process,	Tape calendering
Shipping unit	
Coflow,	1 Mw module
Crossflow,	1/2 Mw module

TABLE 6-20	
ASSUMPTIONS ASSOCIATED WITH PLANT AND FACILITY	
Yearly manufacturing capacity,	200 Mw
Period of manufacture,	10 years
Period of plant construction,	2 years
First year stack output,	0 Mw
Second year stack output,	50 to 100 Mw

TABLE 6-20	
ASSUMPTIONS ASSOCIATED WITH PLANT AND FACILITY (Continued)	
Cost escalation,	About 6 percent/year
Margin,	30 percent on cost
Plant location,	Northeast USA
	Southwest USA
Land and labor rates and taxes,	Tagged to location

TABLE 6-21		
PRODUCTION TARGETS		
	Coflow Design	Crossflow Design
Yearly capacity	200 Mw	200 Mw
Shipping component	1-Mw module	500-kw module
Base shipping module	20 x 50 kw stack	20 x 25 kw stack
Fabricating component	50 kw stack	25 kw stack
Number of stacks per 200 Mwe capacity	4000 x 50 kw stacks	8000 x 25 kw stacks
Number of modules per year	200	400
Number of stacks fabricated per day (300 days/year)	14	28
Fabrication yield	80 percent	80 percent
Production target	16 x 50 kw stacks per day	32 x 25 kw stacks per day

6.3.2 Updated Material Costs

Potential raw material suppliers were identified through several means, including literature surveys, contact with present suppliers, and recommendations from contacts in the industry. Multiple suppliers were sought for most of the materials except for commercially available commodity materials. Well documented quality commodity materials are known to be readily available in large quantities from several suppliers, and therefore only the supplier who is currently used was contacted.

The suppliers contacted are listed in Table 6-22 by the specific materials for which they were considered.

TABLE 6-22	
POTENTIAL SUPPLIERS CONTACTED	
<u>Zirconia</u> AlliedSignal Magnesium electron Rhone-Poulenc TAM TOSH Trans-Tech Z-Tech <u>Lanthanum chromite</u> AlliedSignal Cerac HUA Molycorp Rhone-Poulenc SSC Trans-Tech <u>Lanthanum manganite</u> AlliedSignal Cerac HUA Rhone-Poulenc SSC Trans-Tech	<u>Nickelous oxide</u> Alfa Aldrich Cerac J. T. Baker <u>Anode Additive</u> Meller Optical Alcoa <u>Binder</u> Union Carbide <u>Plasticizer</u> Monsanto <u>Pore Former</u> E M Science

A summary of the estimated bulk prices received from the potential suppliers for each material is presented in Table 6-23. Prices varied substantially for some materials. Broad variations in price were expected for some materials (such as lanthanum manganite and lanthanum chromite) due to uncertainty as to their method of manufacture, yield, economies of scale, and projected raw material costs. In several cases, the estimated prices were substantially higher than those used in the previous manufacturing cost study. For other materials, these prices are lower than those in the cost study. It should be noted that purity level appears to be the prime driving force of price for these materials. In some cases, a slight reduction in the required purity level can reduce the price significantly.

TABLE 6-23

SUPPLIER ESTIMATED BULK PRICES

Material	Previous Cost Study Price, per kg	Supplier	New Estimated Price, per kg
Zirconia	\$9.00	AlliedSignal	\$45.00
		Magnesium Elektron	\$80.00
		Rhone-Poulenc	\$40.00 to \$50.00
		TAM	\$41.00 to \$48.00
		TOSOH	\$55.00 to \$60.00
		Trans-Tech	\$20.00 to \$50.00
		Z-Tech	\$55.00 to \$66.00
Lanthanum chromite	\$80.00	AlliedSignal	\$100.00
		Cerac	\$400.00
		HUA	\$50.00 to \$60.00
		Molycorp	\$26.00 to \$33.00*
		Rhone-Poulenc	\$100.00
		SSC	\$100.00 to \$125.00
		Trans-Tech	\$60.00 to \$5.00
Lanthanum manganite	\$80.00	AlliedSignal	\$100.00
		Cerac	\$400.00
		HUA	\$40.00 to \$50.00
		Rhone-Poulenc	\$100.00
		SSC	\$100.00 to \$125.00
		Trans-Tech	\$50.00 to \$65.00
Nickelous oxide	\$4.50	Aldrich	**
		Alfa	**
		Cerac	\$21.00
		J. T. Baker	\$26.00 to \$35.00
Anode additive	\$1.50	Alcoa	\$2.00
		Meller Optics	\$2.00
Binder	\$3.50	Union Carbide	\$8.00
Plasticizer	\$3.50	Monsanto	\$2.00
Pore former	\$3.50	E M Science	\$20.00
*Required calcining and milling			
**Research lots only			

6.3.2.1 Zirconia

Prices range from \$20/kg to \$80/kg, the average price being \$50/kg. This range is well above the price of \$9/kg that was used in the previous manufacturing cost study. The lower prices were submitted by companies not currently supplying the powders in commercial quantities. Present-day commercial suppliers who undoubtedly have more experience on which to predict future prices tended to submit quotations at the high end of the range.

6.3.2.2 Lanthanum Chromite

Prices for this material range from \$50/kg to \$400/kg, the average price being \$100/kg. The cost of \$80/kg used in the previous cost study falls within this range. The high-end price of \$400/kg was for small-scale batches from a company not capable of scaling up production. The low end price of \$50/kg came from a former supplier who is no longer in business. A price of \$60 to \$75/kg (which is lower than the cost study price) was estimated for this material by Trans-Tech.

6.3.2.3 Lanthanum Manganite

The range of prices for this material was \$40/kg to \$400/kg with the typical price being \$100/kg. The high and low prices for this material correlate closely by supplier with the prices for lanthanum chromite. Trans-Tech estimated \$50 to \$65/kg, which is lower than the \$80/kg price used in the previous cost study.

6.3.2.4 Nickelous Oxide

Prices ranged from \$21/kg to \$35/kg for this material, which are much higher than the \$4.50/kg cost used in the manufacturing cost study. The price of this material is extremely sensitive to purity. A slight decrease in purity level would drop the price substantially.

6.3.2.5 Anode Additive

Prices ranged from \$2/kg to \$20/kg for this material. A price of \$1.50/kg was used in the previous cost study. This material accounts for a small percentage of the total material used in fabricating a fuel cell and therefore has minor impact on the total raw material cost.

6.3.2.6 Binder

The bulk price for the organic binder is \$8/kg, which is more than double the \$3.50/kg price used in the previous cost study. It is doubtful that this price could be reduced further, since the material is already manufactured in bulk and is shipped in truckload lots.

6.3.2.7 Plasticizer

The bulk price for plasticizer is \$2/kg, which is almost half the \$3.50 price used in the previous cost study. The material is currently produced in bulk quantities and can be shipped in tanker truck lots.

6.3.2.8 Pore Former

The bulk price for the grade of pore former currently used in anode and cathode formulations is \$10/kg, which is substantially higher than the \$3.50/kg price used in the previous manufacturing cost study. Cheaper grades of pore former that would perform adequately might be available.

6.3.3 Effects of Utilization of the Thin Electrolyte Approach

The thin electrolyte approach dramatically reduces the usage of yttria-stabilized zirconia, as shown in Table 6-24.

TABLE 6-24					
ELECTROLYTE COMPOSITION AND USAGE					
Tape Material	Weight, %	Coflow		Crossflow	
		Amount Used, Previous Study, kg/yr	Amount Used, This Study, kg/yr	Amount Used, Previous Study, kg/yr	Amount Used, This Study, kg/yr
Yttria-zirconia	84.0	143,086.1	2,862	137,976.0	2,760
Binder	8.0	13,627.3	272	13,140.5	263
Plasticizer	8.0	13,627.3	272	13,627.3	263

6.3.4 Annualized Material Requirements and Costs

Tables 6-25 and 6-26 present the total annual material requirements from the previous study, adjusted for reduced electrolyte usage, and costs based on the "88 prices," the "economic" price from the previous study, and the results of the supplier survey performed under this study. For comparison Tables 6-27 and 6-28 present the results of the previous study.

TABLE 6-25							
MATERIAL REQUIREMENTS FOR THE CROSSFLOW DESIGN AS LOADED							
Material	Weight/yr, kg	'88 Prices		"Economic" Price		Survey Price	
		\$/kg	Cost, \$K	\$/kg	Cost, \$K	\$/kg	Cost, \$K
Ytria-zirconia	72,512	13	943	9	653	50	3,626
SrLaMnO ₃	237,763	275	65,385	80	19,021	100	23,776
SrLaCrO ₃	43,769	275	12,012	80	3,494	100	4,368
NiO	113,807	6	683	4.5	512	25	2,845
Additive	14,160	2.5	335	1.5	21	10	142
Poreformer	27,682	5	138	3.5	97	10	277
Binder	52,714	5	264	3.5	185	8	422
Plasticizer	52,714	5	264	3.5	185	2	105
Solvent	4,000	5	20	3	12	3	12
Ceramic cement	2,000	10	20	6	12	8	16
TOTAL	621,121		79,764		24,192		35,589
(80% effic/fab.mat.)	776,401		99.7M		30.2M		44.4M

TABLE 6-26							
MATERIAL REQUIREMENTS FOR THE COFLOW DESIGN AS LOADED							
Material	Weight/yr, kg	'88 Prices		"Economic" Price		Survey Price	
		\$/kg	Cost, \$K	\$/kg	Cost, \$K	\$/kg	Cost, \$K
Ytria-zirconia	18,346	13	239	9	165	50	917
SrLaMnO ₃	52,780	275	14,515	80	4,222	100	5,280
SrLaCrO ₃	44,971	275	12,367	80	3,598	100	4,500
NiO	25,264	6	152	4.5	114	25	633
Additive	3,143	2.5	8	1.5	5	10	32
Poreformer	6,145	5	31	3.5	22	10	62
Binder	14,906	5	75	3.5	52	8	119
Plasticizer	14,906	5	75	3.5	52	2	30
Solvent	2,000	5	10	3	6	3	6
Ceramic cement	1,000	10	10	6	8	8	8
TOTAL	183,461		27,482		8,244		11,587
(80% effic/fab.mat.)	229,551		34.4M		10.3M		14.5M

TABLE 6-27					
MATERIAL REQUIREMENTS FOR THE CROSSFLOW DESIGN AS LOADED (PREVIOUS STUDY)					
Material	Weight/yr, kg	'88 Prices		"Economic" Price	
		\$/kg	Cost, \$K	\$/kg	Cost, \$K
Ytria-zirconia	207,782.8	13	2,770.8	9	1,918.3
SrLaMnO ₃	237,762.5	275	65,384.7	80	19,021.0
SrLaCrO ₃	43,769.0	275	12,011.7	80	3,494.3
NiO	113,806.8	6	682.8	4.5	512.0
Additive	14,160.3	2.5	35.4	1.5	21.2
Poreformer	27,681.5	5	138.4	3.5	96.9
Binder	65,694.7	5	328.5	3.5	230.0
Plasticizer	65,694.7	5	328.5	3.5	230.0
Solvent	4,000.0	5	20.0	3	12.0
Ceramic cement	2,000.0	10	20.0	6	12.0
TOTAL	782,208.3		81,720.8		25,547.7
(80% eff/c/fab.mat.)	985,000		102.1M		31.9M

TABLE 6-28					
MATERIAL REQUIREMENTS FOR THE COFLOW DESIGN AS LOADED (PREVIOUS STUDY)					
Material	Weight/yr, kg	'88 Prices		"Economic" Price	
		\$/kg	Cost, \$K	\$/kg	Cost, \$K
Ytria-zirconia	158,570.2	13	2,061.4	9	1,427.1
SrLaMnO ₃	52,780.0	275	14,514.5	80	4,222.4
SrLaCrO ₃	44,970.8	275	12,367.0	80	3,597.7
NiO	25,263.6	6	151.6	4.5	113.7
Additive	3,143.4	2.5	7.9	1.5	4.7
Poreformer	6,145.0	5	30.7	3.5	21.5
Binder	28,260.6	5	141.3	3.5	98.9
Plasticizer	28,260.6	5	141.3	3.5	98.9
Solvent	2,000.0	5	10.0	3	6.0
Ceramic cement	1,000.0	10	10.0	6	8.0
TOTAL	350,394.2		29,435.7		9,598.9
(80% eff/c/fab.mat.)	437,993		36.8M		12.0M

6.3.5 Adjusted Annual Operating Costs

Table 6-29 presents the annual operating costs for manufacturing coflow and crossflow stacks in Northeastern and Southwestern U.S. using the updated material costs (adjusted to 80 percent efficiency consistent with previous analyses). For comparison, the annual operating costs using the "economic" materials prices arrived at in the previous study are presented in Table 6-30.

TABLE 6-29				
ANNUAL OPERATING COSTS (UPDATED)				
	Southwest		Northeast	
	Coflow, \$M	Crossflow, \$M	Coflow, \$M	Crossflow, \$M
Labor	6.635	8.701	12.503	14.939
Equipment lease	0.050	0.050	0.050	0.050
Grounds upkeep	0.050	0.050	0.050	0.050
Maintenance	0.250	0.250	0.250	0.250
Raw materials	14.484	44.486	14.484	44.486
Utilities	5.000	5.000	7.000	7.000
Tax and insurance	1.000	1.000	2.000	2.000
Depreciation	1.701	2.096	1.802	2.228
Total	29.170	61.633	38.139	71.003

TABLE 6-30				
ANNUAL OPERATING COSTS (PREVIOUS STUDY)				
	Southwest		Northeast	
	Coflow, \$M	Crossflow, \$M	Coflow, \$M	Crossflow, \$M
Labor	6.635	8.701	12.503	14.939
Equipment lease	0.050	0.050	0.050	0.050
Grounds upkeep	0.050	0.050	0.050	0.050
Maintenance	0.250	0.250	0.250	0.250
Raw materials	11.999	31.874	11.999	31.874
Utilities	5.000	5.000	7.000	7.000
Tax and insurance	1.000	1.000	2.000	2.000
Depreciation	1.701	2.096	1.802	2.228
Total	26.685	49.021	34.654	58.391

7. QUALITY DEVELOPMENT

In this task an evaluation of nondestructive evaluation (NDE) methods was undertaken for the MSOFC, stress analysis, quality control of source materials, and methods of microcrack control.

7.1 EVALUATION OF NDE METHODS

A comprehensive analysis of MSOFC NDE methods was undertaken by Dr. Ellingson of ANL. These results were compiled in a document entitled "nondestructive Characterization Methods For Monolithic Solid Oxide Fuel Cells," ASE Document 93-66149, published April 1, 1993. A summary of the major findings of the study is presented below.

A summary of nondestructive characterization (NDC) of MSOFC suggestions is given in Table 7-1, along with a priority ranking. ASE suggests that the highest priority be given to the development of NDC methods for as-calendered tapes, specifically the trilayer tapes. ASE suggests also that the highest priority be given to the development of acoustic emission to detect the onset of cracking during sintering and to determine maximum outgassing of organics during debinding. Further, ASE suggests that high priority be given to the development of NDC methods for as-calendered single-layer tapes and SrLaMnO_3 and LaCrO_3 powders. ASE suggests that the development of NMR and FTIR spectroscopy be undertaken as NDC methods for as-blended material. This may require a higher priority should recyclable material be combined with new material. There is a concern about the impact of thermal histories and the molecular structure of the polymers.

Although not specifically noted here, if an organic bond material is used as an adhesive to bond A/E/C cells to interconnects, a form of NDC would be necessary to quality these bonds. Sonic resonance methods have recently been developed for similar applications and ASE suggests this be pursued because of the relative inaccessibility of the surfaces for inspection.

7.2 STRESS ANALYSIS OF STACKS

7.2.1 Objective

The objective of the stress analysis task is to predict the stresses incurred during firing and operation of the stack. These data will serve as a basis for determining the relative thickness ratio and other dimensional ratios on composite anode/electrolyte/cathode (A/E/C), single-cell modules, and single-cell stacks.

7.2.2 Analysis of A/E/C Trilayer Composite Tape

To determine the effect of relative thickness of each layer in an A/E/C trilayer composite tape, a constant-thickness (0.01-in) A/E/C trilayer composite disk (see Figure 7-1) was analyzed for the cooldown (2462°F to 77°F) with various thickness ratios. A six-node axisymmetric triangular element (STIF2) of the ANSYS finite-element

TABLE 7-1.

SUMMARY OF POSSIBLE NDC METHODS

Process Step (for material)	Starting Materials (powders) - SrLaMnO ₃ LaCrO ₃	Blended Materials	Flat As-Cast Green Tapes		Corrugated Green Tapes (formed channels)	Debinding	Sintering	Non-mani- folding Sintered Stack	Manifolded Sintered Stack
			Single Layer	Trilayer					
Defect types; Material Character	Powder characteris- tics	Uniformity of blend, surface chemistry	Thickness density	Density, thickness, cracks	Residual stresses		Onset of cracking	Cracks in electrolyte or interconnect delaminations	Gas leakage
NDC Methods Suggested		¹ H NMR spectroscopy	<ul style="list-style-type: none"> • Acoustic microscopy (two-sided) • Low-kV through trans- mission X-ray • Infrared imaging 		FTIR, Raman Spectroscopy		Acoustic emission	Acoustic resonance, optical holography, optical borescopes	Gas pressure by H ₂ leak detection
Priority	High	Medium	Medium	Medium	Medium	High	Highest	Medium	Low

Figure 7-1. Finite Element Model of A/E/C Trilayer Tape

code is used in these analyses. The thermal coefficient of expansion and elastic modules assumed for each material is given in Table 7-2.

Principal tensile stress (SIG1) is given in Table 7-3, while principal compressive stress (SIG3) is given in Table 7-4. The relationship of maximum principal stress in terms of thickness ratio is provided in Figure 7-2.

TABLE 7-2			
THERMAL COEFFICIENT OF EXPANSION, ELASTIC MODULUS, AND STRENGTH			
Item	Coefficient Thermal Expansion, in./in./°F	Elastic Modulus, ksi	Strength, ksi
Anode	6.98×10^{-6}	20,000	15
Electrolyte	6.65×10^{-6}	26,000	27
Cathode	6.73×10^{-6}	20,000	9.1

TABLE 7-3

PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)*
(THICKNESS OF ANODE EQUALS THICKNESS OF CATHODE)

Item	A/E/C Thickness Ratio					
	1:5:1	2:1:2	1:3:1	2:3:2	1:1:1	1:2:1
Electrolyte midplane	-5.5 (8.6)**	-16.4	-7.7 (11.0)	-11.0	-13.2	-9.4 (10.0)**
Anode AE interface	17.3	11.5	15.0	13.9	12.9	14.7
Electrolyte AE interface	-14.3 (10.8)	-19.6	-14.6 (10.6)	-16.7	-18.0	-15.5
Electrolyte CE interface	4.5 (-4.1)	-13.1	-4.6 (6.2)	9.6	9.1	-4.7
Cathode CE interface	8.3	4.4	7.2	5.3	5.2	-6.2
Cathode surface	9.9	7.8	10.2	9.9	9.3	10.2
Anode surface	15.7	2.3 (-4.2)**	11.9	6.6	3.9 (-4.5)**	8.7

*When principal tensile stress (+) is given, principal compressive stress (-) is approximately 0.0 and vice versa.
 ** () = Edge stress

Figures 7-3 through 7-5 show the stress on anode, electrolyte, and cathode respectively, for a 0.01-in.-thick A/E/C trilayer with a 6:2:4 thickness ratio.

TABLE 7-4

PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)*
FOR A/E/C RATIOS OF A/2/C

Item	A/E/C Thickness Ratio								
	1:2:1	1:2:2	2:2:1	2:2:2	2:2:4	4:2:2	4:2:4	4:2:6	6:2:4
Electrolyte midplane	-9.4 (10.0)**	-10.9 (11.4)**	-10.2	-13.2	-14.8	-13.6	-16.4	-17.7	-16.6
Anode AE interface	14.7	15.0	12.8	12.9	13.2	11.9	11.5	11.5	11.2
Electrolyte AE interface	-15.5	-13.8 (11.4)	-17.8	-18.0	-17.2	-19.0	-19.6	-19.8	-20.2
Electrolyte CE interface	-4.7	-8.0 (11.0)	6.9	9.1	-12.6	-8.4	-13.1	-15.5	-13.1
Cathode CE interface	6.2	5.6 (-1.7)	6.2	5.2	6.2	4.3	4.4	5.9	3.1

*When principal tensile stress (+) is given, principal compressive stress (-) is approximately 0.0 and vice versa.
 ** () = Edge stress

TABLE 7-4									
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)* FOR A/E/C RATIOS OF A/2/C (Continued)									
Cathode surface	10.2	6.7	12.0	9.3	6.1	9.2	7.8	7.4	7.3
Anode surface	8.7	12.4	-5.0	3.9 (-4.5)**	8.4	-4.8	2.3 (-4.2)**	-3.9	-4.4
*When principal tensile stress (+) is given, principal compressive stress (-) is approximately 0.0 and vice versa.									
**() = Edge stress									

In addition, stresses were calculated for constant thickness of anode and cathode layer (0.00143 in.) for 1:1:1, 1:3:1, and 1:5:1 thickness ratios of A/E/C trilayer composite tape. The stresses were exactly equal to those given in Table 7-3.

This indicates that cooldown stresses are indifferent to the total thickness of the trilayer tape. However, the stresses are sensitive to the thickness ratio of the layers. Table 7-3 also shows that reducing the thickness of the electrolyte will decrease the stress in the anode and will increase the stress in the cathode.

Figure 7-2. Maximum Principal Stress vs Thickness Ratio

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B-23220

Figure 7-3. Anode Stress for 6:2:4 A/E/C Trilayer Tape

B-23221

Figure 7-4. Electrolyte Stress for the 6:2:4 A/E/C Trilayer Tape

Figure 7-5. Cathode Stress for the 6:2:4 A/E/C Trilayer Tape

7.2.3 Stress Analysis of the Single-Cell Module

The current fundamental building block for the MSOFC stacks is a single-cell module that comprises a cosintered corrugated anode, an anode/electrolyte/cathode trilayer, and a corrugated cathode. A 1.0 x 1.0 single-cell module is analyzed here. The finite element model of the single-cell module is shown in Figure 7-6.

Because of the two planes of symmetry, a quarter of the cell module is modeled. An ANSYS eight-node layered shell (STIF91) is used to model the A/E/C composite tape, and an eight-node isoparametric shell element (STIF93) is used to model the corrugated anode and cathode. Analysis of the cell module indicates high stresses induced in the anode (A/E/C tape) during firing cooldown. The principal tensile stress of the corrugated anode, the corrugated cathode, and the anode in the A/E/C layer tape is illustrated in Figures 7-7 through 7-9, respectively.

Single-cell modules with several A/E/C thickness ratios were analyzed. Table 7-5 and Figure 7-10 show the principal stresses. The results of the analysis indicate that using 1:1:1 trilayer tape in the construction of the single-cell module will reduce the high stress in the anode.

Table 7-6 and Figure 7-11 present the effect of corrugation thickness on the principal stresses. It is apparent from the data shown in Table 7-6 that corrugation thickness has little effect on stresses.

Figure 7-6. Finite Element Model of the Single-Cell Module with Triangular Corrugations

The effect of change in corrugation height in principal stresses is presented in Table 7-7 and Figure 7-12. The analysis results indicate that as the corrugation height increases the stress in the anode corrugation decreases, but the stress in the anode of the trilayer tape increases.

7.2.4 Stress Analysis of the Single-Cell Stack

The single-cell stack finite element model is created by adding flat anode and cathode plates to the single-cell modules. Figure 7-13 shows the finite element model of the single-cell stack with triangular corrugations. In addition, a single-cell stack finite element model was created with rectangular corrugations (Figure 7-14) to evaluate the effect of the change in the shape of the corrugations.

A series of parametric studies has been performed on the two models shown in Figures 7-13 and 7-14 to evaluate the effect of the change in A/E/C thickness ratio, C/A thickness ratio, corrugation height, and corrugation thickness on the principal stresses.

Figure 7-15 presents the principal stresses for the two rectangular corrugation and triangular corrugation stacks as functions of the A/E/C thickness ratio. Analysis results indicate that using 1:1:1 trilayer tape in the construction of the stack is preferable to using 1:5:1 and 1:3:1 ratios. These results are also tabulated in Tables 7-8 and 7-9

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Figure 7-7. Principal Tensile Stress of the Corrugated Anode in the Single-Cell Module (1:1:1 Case)

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Figure 7-8. Principal Tensile Stress of the Corrugated Cathode in the Single-Cell Module (1:1:1 Case)

B-22008

Figure 7-9. Principal Tensile Stress of the Anode in the A/E/C Trilayer Tape of the Single-Cell Module (1:1:1 Case)

for the triangular corrugation and rectangular corrugation stacks respectively. The stresses in general are higher with the rectangular corrugation stack compared to the triangular corrugation stack except for the corrugated anode and corrugated cathode. As shown in Figure 7-15, the difference in the rectangular corrugation and triangular corrugation stress values becomes smaller as the electrolyte over cathode thickness ratio approaches unity.

The effect of the change in cathode over anode thickness ratio in the single-cell stack is also investigated for rectangular corrugation and triangular corrugation. The results of this analysis, shown in Figure 7-16 and Tables 7-10 and 7-11, indicate that the stresses in general are lower with the triangular corrugation stack than the rectangular corrugation stack. Lowering the cathode over anode ratio would additionally result in lower principal stresses.

Figure 7-17 and Tables 7-12 and 7-13 present the results of the change in corrugation thickness for triangular corrugation and rectangular corrugation single-cell stacks. Again, the triangular corrugation type shows lower stresses in most of the stack locations, and as the corrugation thickness increases, the stress levels decrease for both triangular corrugation and rectangular corrugation stack types.

TABLE 7-5

EFFECT OF A/E/C THICKNESS RATIO IN SINGLE-CELL MODULE WITH
TRIANGULAR CORRUGATIONS, PRINCIPAL TENSILE
AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° to 77°F)

Item	A/E/C Thickness Ratio		
	1:5:1	1:3:1	1:1:1
Corrugated anode	12.8	11.6	8.7
	-9.3	-8.7	-7.1
Corrugated cathode	5.2	4.4	2.4
	-4.9	-4.1	-2.3
Anode surface	23.0*	20.9*	15.7*
	0.0	0.0	0.0
Anode AE interface	23.0*	21.0*	16.4*
	0.0	0.0	-0.1
Electrolyte AE interface	0.0	0.0	0.1
	-16.4	-17.8	-20.3
Electrolyte CE interface	2.8	0.6	0.1
	-11.5	-12.8	-16.6
Cathode CE interface	10.3	8.3	2.3
	-0.1	-1.6	-4.6
Cathode surface	11.5	10.2	6.0
	-0.1	-1.3	-3.9

*Stress values exceed strength.

Note:

Cell dimension = 1.0 in. x 1.0 in.

Corrugation height = 0.05 in.

No. of corrugations per in. = 10

Corrugation thickness = 0.01 in.

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Figure 7-10. Effect of A/E/C Thickness Ratio in Single-Cell Module with Triangular Corrugations

TABLE 7-6

**EFFECT OF CORRUGATION THICKNESS IN SINGLE-CELL
MODULE WITH TRIANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPREHENSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)**

Item	Thickness of Corrugation		
	0.003	0.005	0.01
Corrugated anode	10.5	9.8	8.7
	-8.2	-7.5	-7.1
Corrugated cathode	3.3	2.3	2.4
	-2.3	-2.3	-2.3
Anode surface	16.1*	15.8*	15.7*
	0.0	0.0	0.0
Anode AE interface	15.4*	15.4*	16.4*
	0.0	0.0	-0.1
Electrolyte AE interface	0.0	0.0	0.1
	-18.4	-19.2	-20.3
Electrolyte CE interface	0.1	0.1	0.1
	-14.5	-14.8	-16.6
Cathode CE interface	1.8	2.1	2.3
	-3.0	-3.2	-4.6
Cathode surface	6.9	6.6	6.0
	-3.8	-3.9	-3.9

*Stress values exceed strength.

Note:
Cell dimension = 1.0 in. x 1.0 in.
A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 10
Corrugation height = 0.05 in.

Figure 7-11. Effect of Corrugation Thickness in Single-Cell
Module with Triangular Corrugations

TABLE 7-7

**EFFECT OF CORRUGATION HEIGHT IN SINGLE-CELL MODULE WITH
TRIANGULAR CORRUGATIONS, PRINCIPAL TENSILE AND
COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)**

Item	Corrugation Height			
	0.01	0.03	0.05	0.10
Corrugated anode	17.9*	9.1	8.7	7.6
	-11.8	-9.1	-7.1	-4.7
Corrugated cathode	9.5	5.1	2.4	0.6
	-8.9	-4.7	-2.3	-0.8
Anode surface	11.6	14.8	15.7*	16.1*
	0.0	0.0	0.0	0.0
Anode AE interface	14.5	15.8*	16.4*	16.9*
	0.0	0.0	-0.1	-0.0
Electrolyte AE interface	0.0	0.0	0.1	0.0
	-23.5	-20.1	-20.3	-20.3
Electrolyte CE interface	0.0	0.1	0.1	0.1
	-18.2	-16.8	-16.6	-17.7
Cathode CE interface	2.5	2.5	2.3	2.2
	-5.7	-4.7	-4.6	-5.4
Cathode surface	7.9	6.7	6.0	5.6
	-2.7	-3.3	-3.9	-5.3

*Stress values exceed strength.

Note:

Cell dimension = 1.0 in. x 1.0 in.

A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 10

Corrugation height = 0.01 in.

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Figure 7-12. Effect of Corrugation Height in Single-Cell Module with Triangular Corrugations

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Figure 7-13. Finite Element Model of the Single-Cell Stack with Triangular Corrugations

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Figure 7-14. Finite Element Model of the Single-Cell Stack with Rectangular Corrugations

Figure 7-15. Effect of A/E/C Thickness Ratio in Single-Cell Stack with Rectangular and Triangular Corrugations

The effects of the change in corrugation height in single-cell stacks with rectangular corrugations and triangular corrugations are presented in Figure 7-18 and Tables 7-14 and 7-15. The stress results are lower for most of the locations within the triangular corrugation stack compared with those of the rectangular corrugation stack. As shown in Figure 7-18, different layers of rectangular corrugation and triangular corrugation stacks behave inconsistently as the corrugation height increases.

Comparison of the stresses induced in the single-cell stack and in the single-cell module with triangular corrugations has been performed. The results, presented in Figures 7-19 through 7-21, indicate that the stress levels are higher in the single-cell stack than in the single-cell module, but all behave in the same way as functions of cathode thickness ratio, corrugation thickness, and corrugation height.

7.2.5 Conclusions

Stresses caused by uniform cooldown in a trilayer A/E/C tape are insensitive to the total thickness of the tape. However, the stresses are sensitive to the thickness ratio of the layers.

TABLE 7-8

EFFECT OF A/E/C THICKNESS RATIO IN SINGLE-CELL STACK
WITH TRIANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	A/E/C Thickness Ratio		
	1:5:1	1:3:1	1:1:1
Corrugated anode	17.0*	15.0	10.1
	-8.8	-7.7	-5.1
Corrugated cathode	11.6	9.6	4.7
	-6.3	-5.3	-4.3
Anode surface	24.6*	22.0*	15.8*
	0.0	0.0	0.0
Anode AE interface	23.9*	21.3*	15.9*
	-0.1	-0.1	-0.2
Electrolyte AE interface	0.8	0.5	0.2
	-24.1	-24.2	-24.0
Electrolyte CE interface	4.9	1.7	0.2
	-19.7	-19.4	-20.1
Cathode CE interface	12.0	9.5	2.7
	-7.0	-6.8	-7.2
Cathode surface	13.7	12.0	7.1
	-7.7	-7.3	-6.8
Flat anode	6.2	5.4	3.5
	-4.9	-4.5	-3.4
Flat cathode	5.9	5.2	3.5
	0.0	0.0	-0.1

* Stress values exceed strength.

Note:

Cell dimension = 1.0 in. x 1.0 in.
Corrugation height = 0.05 in.

No. of corrugations per in. = 10
Corrugation thickness = 0.01 in.

TABLE 7-9

EFFECT OF A/E/C THICKNESS RATIO IN SINGLE-CELL STACK
WITH RECTANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	A/E/C Thickness Ratio		
	1:5:1	1:3:1	1:1:1
Corrugated anode	12.7	11.6	9.9
	-15.9	-14.2	-9.8
Corrugated cathode	8.1	6.8	3.9
	-8.8	-7.6	-6.9
Anode surface	27.0*	23.5*	15.5*
	-7.0	-6.7	-6.2
Anode AE interface	26.9*	23.9*	17.3*
	-0.3	-0.2	-0.2
Electrolyte AE interface	2.0	0.3	0.4
	-25.7	-26.2	-27.5*
Electrolyte CE interface	3.5	1.0	0.3
	-26.3	-26.7	-27.7*
Cathode CE interface	10.9	9.0	3.9
	-12.1	-12.4	-13.2
Cathode surface	12.9	13.2	13.6
	-11.9	-12.3	-13.2
Flat anode	2.8	2.5	2.1
	-3.0	-2.8	-2.4
Flat cathode	2.7	2.7	2.6
	-2.0	-1.6	-1.3

* Stress values exceed strength.

Note:

Cell dimension = 0.5 in. x 0.5 in.
Corrugation height = 0.10 in.

No. of corrugations per in. = 12
Corrugation thickness = 0.01 in.

Figure 7-16. Effect of C/A Thickness Ratio in Single-Cell Stack with Rectangular and Triangular Corrugations

Cooldown analysis indicates that the 1:1:2 thickness ratio A/E/C trilayer tape has a better probability of survival than the tapes of other thickness ratios. Cracks or flaws through the thickness of the trilayer A/E/C tape are more critical than the longitudinal ones through electrolyte midplane.

Preliminary cooldown analysis is in progress on the single-cell module and the single-cell stack. Results of this analysis will be published in a future report.

Preliminary cooldown analysis of the single-cell stacks with rectangular corrugations does not show any advantage over triangular corrugations.

Introducing uniform porosity and possibly reducing porosity will increase strength of the anode and cathode and will reduce irregular, excessive shrinkage spots. This will lead to better probability of stack survival.

TABLE 7-10

EFFECT OF A/C THICKNESS RATIO IN SINGLE-CELL STACK
WITH TRIANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	A/E/C Thickness Ratio		
	2:1:1	1:1:2	1:1:1
Corrugated anode	7.0	10.6	10.1
	-3.4	-5.3	-5.1
Corrugated cathode	3.1	5.0	4.7
	-4.6	-4.2	-4.3
Anode surface	12.1	17.0*	15.8*
	0.0	0.0	0.0
Anode AE interface	13.2	16.8*	15.9*
	-0.2	-0.1	-0.2
Electrolyte AE interface	1.0	0.2	0.2
	-21.5	-24.0	-24.0
Electrolyte CE interface	0.1	0.3	0.2
	-21.3	-22.9	-20.1
Cathode CE interface	0.3	1.3	2.7
	-8.2	-8.6	-7.2
Cathode surface	3.4	6.4	7.1
	-8.4	-7.7	-6.8
Flat anode	2.0	3.7	3.5
	-2.7	-3.4	-3.4
Flat cathode	3.0	3.8	3.5
	-0.5	-0.0	-0.1

* Stress values exceed strength.

Note:

Cell dimension = 1.0 in. x 1.0 in.

Corrugation height = 0.05 in.

No. of corrugations per in. = 10

Corrugation thickness = 0.01 in.

TABLE 7-11

EFFECT OF A/E/C THICKNESS RATIO IN SINGLE-CELL STACK
WITH RECTANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	A/E/C Thickness Ratio		
	2:1:1	1:1:2	1:1:1
Corrugated anode	10.3	12.5	12.3
	-8.4	-12.2	-12.0
Corrugated cathode	5.9	8.7	8.4
	-8.7	-9.4	-9.3
Anode surface	13.1	17.7*	15.4*
	9.9	6.2	6.2
Anode AE interface	14.5	18.3*	17.2*
	-0.4	-0.1	-0.2
Electrolyte AE interface	0.4	0.2	0.3
	-27.4*	-26.2	-26.4
Electrolyte CE interface	0.2	0.2	0.3
	-27.5*	-26.4	-26.5
Cathode CE interface	5.2	1.8	3.9
	-13.0	-12.0	-12.2
Cathode surface	15.1	8.6	13.6
	-12.1	-11.4	-11.4
Flat anode	2.9	3.5	3.5
	-3.5	-3.6	-3.6
Flat cathode	4.1	2.4	4.5
	-2.1	-1.7	-1.7

*Stress values exceed strength.

Note:

Cell dimension = 0.5 in. x 0.5 in.

Corrugation height = 0.05 in.

No. of corrugations per in. = 12

Corrugation thickness = 0.01 in.

TABLE 7-12

**EFFECT OF CORRUGATION THICKNESS IN SINGLE-CELL STACK
WITH TRIANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)**

Item	Thickness of Corrugation		
	0.003	0.005	0.01
Corrugated anode	13.5 -3.7	12.1 -3.6	10.1 -5.1
Corrugated cathode	9.0 -4.7	7.3 -4.4	4.7 -4.3
Anode surface	17.2* 0.0	16.6* 0.0	15.8* 0.0
Anode AE interface	15.6* -0.2	15.9* -0.2	15.9* -0.2
Electrolyte AE interface	0.3 -22.6	0.3 -23.4	0.2 -24.0
Electrolyte CE interface	0.3 -17.8	0.4 -18.7	0.2 -20.1
Cathode CE interface	3.2 -5.5	3.3 -6.2	2.7 -7.2
Cathode surface	10.4 -6.3	9.7 -6.4	7.1 -6.8
Flat anode	2.7 -3.3	2.8 -3.4	3.5 -3.4
Flat cathode	3.2 -0.2	3.5 -0.3	3.8 -0.1

*Stress values exceed strength.

Note:

Cell dimension = 1.0 in. x 1.0 in.
A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 10
Corrugation height = 0.05 in.

TABLE 7-13

EFFECT OF CORRUGATION THICKNESS RATIO IN SINGLE-CELL
STACK WITH RECTANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	Thickness of Corrugation		
	0.003	0.005	0.01
Corrugated anode	13.9	13.5	12.3
	-14.5	-16.0*	-12.0
Corrugated cathode	13.3	11.3	8.4
	-11.6	-11.0	-9.3
Anode surface	16.7*	15.7*	15.4*
	-1.9	-4.3	-6.2
Anode AE interface	15.2*	15.9*	17.2*
	-0.2	-0.2	-0.2
Electrolyte AE interface	0.1	0.2	0.3
	-21.6	-23.8	-26.4
Electrolyte CE interface	0.1	0.2	0.3
	-21.9	-24.2	-26.5
Cathode CE interface	3.6	3.6	3.9
	-8.9	-10.5	-12.2
Cathode surface	13.1	13.3	13.6
	-9.7	-11.1	-11.4
Flat anode	1.9	2.1	3.5
	-2.5	-2.8	-3.6
Flat cathode	2.1	2.9	4.5
	-1.7	-1.6	-1.7

* Stress values exceed strength.

Note:

Cell dimension = 0.5 in. x 0.5 in.
A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 12
Corrugation height = 0.05 in.

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Figure 7-17. Effect of Corrugation Thickness in Single-Cell Stack with Triangular and Rectangular Corrugations

B-22013

Figure 7-18. Effect of Corrugation Height in Single-Cell Stack with Triangular and Rectangular Corrugations

TABLE 7-14

**EFFECT OF CORRUGATION HEIGHT IN SINGLE-CELL STACK
WITH TRIANGULAR TYPE CORRUGATION,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)**

Item	Corrugation Height			
	0.01	0.03	0.05	0.10
Corrugated anode	17.5*	10.6	10.1	9.0
	-11.2	-7.3	-5.1	-3.0
Corrugated cathode	7.9	4.7	4.7	4.9
	-10.0	-5.6	-4.3	-3.1
Anode surface	11.2	14.5	15.8*	16.7*
	0.0	0.0	0.0	0.0
Anode AE interface	14.4	15.2*	15.9*	16.9*
	-0.1	-0.1	-0.2	-0.2
Electrolyte AE interface	0.0	0.1	0.2	0.4
	-25.1	-24.1	-24.0	-24.0
Electrolyte CE interface	0.0	0.2	0.2	0.3
	-19.7	-19.8	-20.1	-20.5
Cathode CE interface	2.5	2.8	2.7	2.8
	-6.8	-6.9	-7.2	-7.5
Cathode surface	8.4	7.6	7.1	7.3
	-3.8	-6.1	-6.8	-7.1
Flat anode	6.6	3.9	3.5	2.8
	-5.9	-1.4	-3.4	-2.6
Flat cathode	6.9	4.7	3.8	2.6
	-3.1	-0.2	-0.1	0.0

*Stress values exceed strength.

Note:

Cell dimensions = 1.0 in. x 1.0 in.

A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 10

Corrugation thickness = 0.01 in.

TABLE 7-15

EFFECT OF CORRUGATION HEIGHT IN SINGLE-CELL STACK
WITH RECTANGULAR CORRUGATIONS,
PRINCIPAL TENSILE AND COMPRESSIVE STRESSES (KSI)
(STRESSES DUE TO COOLDOWN: 2462° TO 77°F)

Item	Corrugation Height			
	0.01	0.03	0.05	0.10
Corrugated anode	13.5*	13.8	12.3	9.9
	-13.8	-13.3	-12.0	-9.8
Corrugated cathode	6.7	10.3	8.4	3.9
	-7.9	-10.2	-9.3	-6.9
Anode surface	15.1*	15.1*	15.4*	15.5*
	-5.7	-5.8	6.2	-6.2
Anode AE interface	16.7*	16.9*	17.2*	17.3*
	-0.1	-0.2	-0.2	-0.2
Electrolyte AE interface	0.3	0.3	0.3	0.4
	-23.2	-24.9	-26.4	-27.5*
Electrolyte CE interface	0.3	0.3	0.3	0.3
	-21.7	-24.6	-26.5	-27.7*
Cathode CE interface	4.0	4.0	3.9	3.9
	-8.3	-10.8	-12.2	-13.2
Cathode surface	14.0	13.8	13.6	13.6
	-6.4	-8.6	-11.4	-13.2
Flat anode	7.2	4.7	3.5	2.1
	-6.7	-4.8	-3.6	-2.4
Flat cathode	5.9	5.5	4.5	2.6
	-5.1	-1.5	-1.7	1.3

* Stress values exceed strength.

Note:

Cell dimensions = 0.5 in. x 0.5 in.

A/E/C thickness ratio = 1:1:1

No. of corrugations per in. = 12

Corrugation thickness = 0.01 in.

B-22014

Figure 7-19. Effect of Corrugation Thickness in Single-Cell Module and Stack (Triangular Corrugation)

B-22015

Figure 7-20. Effect of Corrugation Height in Single-Cell Module and Stack (Triangular Corrugation)

B-23403

Figure 7-21. Effect of A/E/C Thickness Ratio in Single-Cell Module and Stack (Triangular Corrugation)

TABLE 7-16			
ROBUST DESIGN EXPERIMENT, AUTOMATED FINITE ELEMENT MODEL			
Item	Level		
Anode thickness A/E/C, in.	0.003	0.005	0.007
Cathode thickness A/E/C, in.	0.003	0.005	0.007
Electrolyte thickness A/E/C, in.	0.003	0.005	0.007
Corrugation thickness, in.	0.005	0.01	0.015
Corrugation height, in.	0.05	0.1	0.15
Flat anode thickness, in.	0.005	0.01	0.015
Flat cathode thickness, in.	0.005	0.01	0.015
Shape of corrugation	Triangular	Rectangular	NA

7.2.6 Robust Design Study

A robust design experimental study was performed for the single-cell stack crossflow monolithic solid oxide fuel cell (MSOFC) shown in Figure 7-22. The single-cell stack is a combination of a cathode plate, corrugated cathode, tri-layer, corrugated anode, and an anode plate stacked up in series, as shown in Figure 7-22. The factors used for the robust design study are anode thickness, cathode thickness, electrolyte thickness, corrugation thickness, corrugation height, flat anode thickness, flat cathode thickness, and the trapezoid side ratio. These factors and their associated values used for this study are listed in Table 7-17.

Figure 7-22. Crossflow Monolithic Solid Oxide Fuel Cell

TABLE 7-17			
ASSIGNED FACTOR VALUES			
Factors	Levels		
Anode thickness A/E/C	0.003	0.005	0.007
Cathode thickness A/E/C	0.003	0.005	0.007
Electrolyte thickness A/E/C	0.003	0.005	0.007
Corrugation thickness	0.005	0.01	0.015
Corrugation height	0.05	0.1	0.15
Flat anode thickness	0.005	0.01	0.015
Flat cathode thickness	0.005	0.01	0.015
Trapezoidal side ratio	0.2	0.5	

During the third quarter, a similar experiment was performed. The only difference was corrugation shape was a factor instead of trapezoid side ratio. The results of this study are reported in ASE Document 90-63592(16).

An L_{18} orthogonal array experimental analysis using these factors was performed to determine the best combination of the factors that would result in the lowest stresses induced in the single-cell stack. A parametric finite element model of the single-cell stack with the trapezoidal corrugation was constructed for this study. The 18 structured numerical experiments required for the robust design were run using the described finite element model on ANSYS. These 18 experiments are listed in Table 7-18.

The results of each run were posted for different parts of the single-cell stack. After a careful comparison, the major stress items were selected for plotting purposes: corrugated anode; corrugated cathode, anode, cathode; and electrolyte. The maximum tensile stresses were utilized, except for the electrolyte where the maximum compressive stress was used. These stress values were divided by the individual mean strength values (cathode: 9 ksi, anode: 15 ksi, electrolyte: 27 ksi) to obtain the stress ratios, which, in turn were plotted for the robust design evaluation. The principal stresses associated with each selected layer of the single-cell stack for each experiment are listed in Table 7-19. The factor plots presented in Figures 7-23 and 7-24 are the results of the stress ratios plotted versus the robust design factors. Factor plots are constructed by averaging all the experiments performed for that factor. For example, to plot electrolyte stress for anode thickness of 0.003 in. (anode thickness factor plot), electrolyte stresses of all the experiments with an anode thickness of 0.003 in. would be averaged, etc. In general, most of the items plotted in Figure 7-23 behave differently to a factor change, making it difficult to select the best value for a factor. To minimize this problem, a quadratic mean procedure is utilized to reduce these five stress items to one. The plot of the quadratic mean is presented in Figure 7-24.

TABLE 7-18

L₁₈ ORTHOGONAL ARRAY EXPERIMENT

No.	AT	ET	CT	COT	COH	FAT	FCT	SR
1	0.003	0.003	0.003	0.005	0.05	0.005	0.005	0.2
2	0.003	0.005	0.005	0.010	0.10	0.010	0.010	0.2
3	0.003	0.007	0.007	0.015	0.15	0.015	0.015	0.2
4	0.005	0.003	0.003	0.010	0.10	0.015	0.015	0.2
5	0.005	0.005	0.005	0.015	0.15	0.005	0.005	0.2
6	0.005	0.007	0.007	0.005	0.05	0.010	0.010	0.2
7	0.007	0.005	0.003	0.005	0.15	0.010	0.015	0.2
8	0.007	0.007	0.005	0.010	0.05	0.015	0.005	0.2
9	0.007	0.003	0.007	0.015	0.10	0.005	0.010	0.2
10	0.003	0.007	0.003	0.015	0.10	0.010	0.005	0.5
11	0.003	0.003	0.005	0.005	0.15	0.015	0.010	0.5
12	0.003	0.005	0.007	0.010	0.05	0.005	0.015	0.5
13	0.005	0.005	0.003	0.015	0.05	0.015	0.010	0.5
14	0.005	0.007	0.005	0.005	0.10	0.005	0.015	0.5
15	0.005	0.003	0.007	0.01	0.15	0.01	0.005	0.5
16	0.007	0.007	0.003	0.010	0.15	0.005	0.01	0.5
17	0.007	0.003	0.005	0.015	0.05	0.01	0.015	0.5
18	0.007	0.005	0.007	0.005	0.10	0.015	0.005	0.5

TABLE 7-19

ROBUST DESIGN EXPERIMENT RESULTS - TRAPEZOID

No.	Factors								Stress, ksi				
	AT	ET	CT	COT	COH	FAT	FCT	SR	E	C	AC	CC	A
1	0.003	0.003	0.003	0.005	0.05	0.005	0.005	0.2	-20.9	12.4	12.4	15.5	19.4
2	0.003	0.005	0.005	0.010	0.10	0.010	0.010	0.2	-21.5	9.6	12.6	8.7	22.0
3	0.003	0.007	0.007	0.015	0.15	0.015	0.015	0.2	-21.7	7.3	12.3	5.7	23.5
4	0.005	0.003	0.003	0.010	0.10	0.015	0.015	0.2	-23.0	13.8	8.2	8.1	20.0
5	0.005	0.005	0.005	0.015	0.15	0.005	0.005	0.2	-23.1	12.6	8.8	7.2	21.9
6	0.005	0.007	0.007	0.005	0.05	0.010	0.010	0.2	-21.1	9.8	13.8	21.7	15.1
7	0.007	0.005	0.003	0.005	0.15	0.010	0.015	0.2	-21.1	14.3	9.2	17.4	17.5
8	0.007	0.007	0.005	0.010	0.05	0.015	0.005	0.2	-21.0	13.6	10.9	17.1	15.2
9	0.007	0.003	0.007	0.015	0.10	0.005	0.010	0.2	-24.0	10.4	7.5	9.0	17.4
10	0.003	0.007	0.003	0.015	0.10	0.010	0.005	0.5	-20.9	13.2	16.0	8.2	23.2
11	0.003	0.003	0.005	0.005	0.15	0.015	0.010	0.5	-20.3	8.8	9.7	6.3	20.6
12	0.003	0.005	0.007	0.010	0.05	0.005	0.015	0.5	-21.1	7.8	19.6	13.5	20.1
13	0.005	0.005	0.003	0.015	0.05	0.015	0.010	0.5	-22.4	14.6	13.8	9.3	16.9
14	0.005	0.007	0.005	0.005	0.10	0.005	0.015	0.5	-18.3	12.1	13.7	16.0	19.7
15	0.005	0.003	0.007	0.01	0.15	0.01	0.005	0.5	-22.5	9.4	8.8	7.0	18.3
16	0.007	0.007	0.003	0.010	0.15	0.005	0.01	0.5	-20.3	15.5	10.1	11.3	18.5
17	0.007	0.003	0.005	0.015	0.05	0.01	0.015	0.5	-24.1	11.1	9.8	11.1	13.6
18	0.007	0.005	0.007	0.005	0.10	0.015	0.005	0.5	-20.3	10.6	10.9	17.7	15.5

Figure 7-23. Stress Ratio Factor Plot

Figure 7-23. (Continued)

Figure 7-24. Quadratic Mean Stress Ratio Factor Plots

○ NON-TRAPEZOIDAL
● TRAPEZOIDAL

Figure 7-24. (Continued)

From an evaluation of the stress ratios, two sets of factors were selected as best and are shown below.

<u>Factor</u>	<u>Figure 7-23, in.</u>	<u>Figure 7-24, in.</u>
Trapezoid side ratio	0.5	0.5
Anode thickness	0.005	0.003
Electrolyte thickness	0.003	0.003
Cathode thickness	0.005	0.005
Corrugation thickness	0.015	0.015
Corrugation height	0.100	0.150
Flat anode thickness	0.015	0.015
Flat cathode thickness	0.010	0.010

A thin-electrolyte approach was evaluated via the cooldown stress model. Table 7-20 compares the stresses for various thin-electrolyte approaches vs the current baseline (2:1:1) and 1:5:1 A/E/CE geometries. A/E/CE anode and cathode stresses are greatly reduced in such an approach. The highest stresses were incurred in the corrugated cathode.

The current MSOFC finite-element stress model is being expanded to include the "heat up" portion of the firing cycle and multicell stack thermal processing. The heat-up modeling will include the effects of constraint weights, frictional effects, and heat-up temperature profile. The effect of mechanical "creep" in maintaining stack shape and relieving stress will be evaluated. The model will include the entire thermal processing cycle for a two-cell stack. Recommendations for improved designs, processes, and material properties will be provided.

Plans also call for modeling the effect of manifolding on stack integrity, as it is suspected that the stacks may be damaged as the result of the manifolding materials or processes.

7.3 QUALITY CONTROL OF SOURCE MATERIALS

The objective of this task is to evaluate the characteristics and quality of source materials for use in the fabrication of the MSOFC. Variations in material characteristics and their effect on MSOFC fabrication were quantified, and the acceptable quality of source materials was specified.

The materials studied were lanthanum manganite and lanthanum chromite. The materials from various suppliers were evaluated in the manner described below.

7.3.1 Lanthanum Manganite

La_{0.89}Sr_{0.10}MnO₃ (LM) supplied by Trans-Tech has been evaluated as a replacement for the same material from HUA Associates, a company no longer in the powder supply

TABLE 7-20

STRESS ANALYSIS RESULTS

Factor	Thin Electrolytes						2:1:1	1:5:1
	0.2	0.005	0.0002	0.005	0.010	0.050	0.2	0.0014
Trapezoid side ratio	0.2	0.005	0.0002	0.005	0.010	0.050	0.2	0.0014
Anode thickness	0.005	0.0005	0.0002	0.005	0.010	0.050	0.005	0.0072
Electrolyte thickness	0.0005	0.0002	0.0005	0.003	0.010	0.050	0.0025	0.0014
Cathode thickness	0.005	0.005	0.010	0.010	0.050	0.010	0.010	0.010
Corrugation thickness	0.010	0.050	0.010	0.050	0.010	0.010	0.050	0.050
Corrugation height	0.050	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Flat anode thickness	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Flat cathode thickness	0.010	0.010	0.010	0.010	0.010	0.010	0.010	0.010
Location	Stress						Ksi	Ksi
	Ksi	Ksi	Ksi	Ksi	Ksi	Ksi		
Anode	15.6	15.3	12.9	12.8	18.1	24.8		
Electrolyte	-25.1	-25.6	-29.9	-27.1	-25.0	-21.2		
Cathode	9.2(-13.9)	9.1(-14.6)	7.5(-16.4)	8.0(-14.5)	13.3	12.5		
Corrugated cathode	11.3	11.3	12.6	13.2	11.4	11.7		
Corrugated anode	6.9(-12.2)	6.7(-11.7)	6.1(-10.5)	6.1(-12.4)	8.0(-14.5)	19.4(-20.7)		

business. Trans-Tech was able to tailor the powder to material specification requirements.

The HUA powder was received in a very reactive form with a high surface area. The powder was then calcined before use in cathode and intermediate formulations. Calcined powder has been used in the cathode formulation to tailor cathode density (porosity) and firing shrinkage. Calcined HUA LM powder was also ball milled to break up particle agglomerates formed during calcination.

Rhone-Poulenc has also provided a sample of LM powder to be evaluated for potential use in the MSOFC. Its powder was found to have a surface area of $4.4 \text{ m}^2/\text{g}$, which is higher than the specification requires. This powder was used to make an intermediate batch (CE01311-2), which showed much lower open sintered porosity than the baseline for the study. An attempt to make a cathode batch with this material was unsuccessful. The high surface area of the powder is believed to be the source of the problem.

Three more lots of $\text{La}_{.89}\text{Sr}_{.10}\text{MnO}_3$ powder were received from Rhone-Poulenc, Inc. The particle size distributions and surface areas of the three lots are shown in Figure 7-25. In terms of particle size distribution and surface area, lot NBK-C2B most closely matches the present baseline $\text{La}_{.89}\text{Sr}_{.10}\text{MnO}_3$ powder supplied by Trans-Tech, Inc. Powders from all three Rhone-Poulenc lots have been made into cathode and cathode/electrolyte intermediate batches.

7.3.2 Lanthanum Chromite

Lanthanum chromite powders from a variety of suppliers were evaluated, specifically Trans-Tech, SSC Inc., Molycorp, and Battelle Northwest Laboratory. Work also continued on the evaluation of the material supplied from AlliedSignal Research and Technology (ASR&T) and a new effort was initiated to define and explore new areas of interconnect development.

Doped lanthanum chromite material was received from all of the suppliers listed above. Lanthanum chromite doped with calcium and cobalt was received from Trans-Tech and SSC and strontium-doped lanthanum chromite was received from Molycorp and Battelle. With the exception of the Molycorp materials all the as-received powders were prereacted to form the desired endproduct, lanthanum chromite. The powder received from Molycorp was received as a wet cake, the proportions of lanthanum and chromium were chemically correct; however, the proper phases were not formed. The as-received powders underwent analysis to determine the surface area. The average particle size was calculated using value for surface area as shown in Equation (1).

$$ps = 6 / [(sa \text{ (sq/m)}) (6.77 \text{ g/cu cm}) (10^6 \text{ cu cm/cm m})] \quad (1)$$

where ps is the particle size and sa is the surface area. The results are summarized in Table 7-21.

received 7-17-91, measured w/ dispersant

Figure 7-25. Particle Size Distribution of Rhone-Poulenc Sr-LaMnO₃

TABLE 7-21			
SURFACE AREA AND PARTICLE SIZE FOR AS-RECEIVED POWDERS			
Supplier	Composition	Surface Area (sq m/g)	Particle Size*, nm
Trans-Tech	La(Ca)Cr(Co)O ³	1.30	681
SSC Inc.	La(Ca)Cr(Co)O ³	4.83	182
Battelle	La(Sr)CrO ³	20.5	43
Molycorp**	La(Sr)CrO ³	72.5	12
* Calculated			
** Dried powder; not calcined.			

The wet cake received from Molycorp was dried for 24 hr at 100.5°C. The resulting dried cake was granulated and calcined at both 900.5 and 1000.5°C for 1, 5 and 10 hr to determine the temperature and time necessary to achieve an average surface area between 2 and 5 microns. The resulting surface area as a function of both calcination temperature and time are shown in Figure 7-26. A tape was made with this powder and sintered at temperatures between 1350.5°C and 1550.5°C for 1 hr. The highest sintered density achieved was approximately 70 percent of theoretical.

The LaCrO₃ powder received from the Battelle Northwest Laboratory was too fine to be made into a tape or pressed into a bulk shape for evaluation. The powder was therefore calcined at 1000.5°C for 10 hr and the resultant surface area was 1.6 sq m/g, sufficient to form either a tape or bulk shape. The calcined powder was pressed into disks and sintered at 1500.5 and 1550.5 for 1 hr. No densification was observed in this material at either temperature. The maximum sintered density was equivalent to the initial green density, about 50 percent of theoretical.

The as-received powder from SSC Inc. was used to make a tape. However either due to the high surface area or possible to a large pore volume within the powder, a tape could not be formed using a 50-volume-percent solids loading. The powder was calcined to burn off any residual binder and then heated to a higher temperature to decrease the surface area and pore volume. The resulting powder had a surface area of 2 m²/g and was easily fabricated into a tape. These tapes attained near theoretical densities (99 percent) when sintered at 1350.5°C for 1 hr, as indicated in the SEM evaluation of a fracture surface (Figure 7-27). Further SEM examination indicated the presence of a liquid phase on the sample surface. This is believed to be CaCrO₄, which was found in the initial powder x-ray diffraction pattern.

Tapes were readily fabricated using the as-received powder from Trans-Tech. The tapes, when sintered at 1350.5°C for 1 hr, achieved densities approaching 94 percent of theoretical, shown in Figure 7-28. The lower density observed in these samples, as

Figure 7-26. Calcination Study of Unocal Sr.LaCO_3 as a Function of Time and Temperature

Figure 7-27. Fracture Surface of Ca,Co.LaCO_3 Sintered at 1350°C for 1 Hr. Interconnect from SSC, Inc.

compared to the SSC specimens, is believed to be due to a smaller concentration of liquid phase being present in the sample during sintering.

The morphologies of the powders from each of the suppliers are shown in Figure 7-29. Figure 7-29(a) shows the powder received from SSC. The hollow spherical agglomerates in the as-received powder are characteristic of the morphology of powder synthesized by the spray pyrolysis method. The SSC powder is soft and easily deformable, making it quite flexible for any fabrication technique.

Trans-Tech powder is shown in Figure 7-29(b). This powder has an average particle size of approximately 0.7μ ; however, the size of some particles is much larger, as seen in Figure 7-29(b). The powder is prepared by solid-state reaction of the constituent oxides and results in large hard particles. The particles need to be broken down to increase the reactivity of the powder prior to sintering. Figure 7-29(c) shows the powder produced by HUA. This powder is characterized by small particles that form large hard agglomerates during calcination. The ASR&T powder, prepared by an aerogel method, has a very fine particle size, and forms soft friable agglomerates (Figure 7-29(d)). The surface area of this material needs to be decreased through calcination before it can be fully utilized in the tape calendaring process.

The interconnect powders received from the suppliers mentioned above were made into single layer tapes and were evaluated for the degree of densification at 1400°C (see Table 7-22). The densities of the various samples were determined by a water immersion technique and are compared against the area density determined

Figure 7-28. Fracture Surface of Ca,Co.LaCO_3 Sintered at 1350°C for 1 Hr. Interconnect from Trans-Tech

F-63042

(a) SSC

(b) Trans-Tech

10μm

(c) HUA

(d) ASR&T

Figure 7-29. Surface Morphologies of As-Received Powders

F-60097

from polished and thermally etched surfaces. The areal density, derived from polished cross sections of the sample, is considered to be more accurate because of less error in the estimation.

TABLE 7-22		
DENSITY OF SINGLE-LAYER TAPES SINTERED AT 1400°C FOR 1 HR		
Supplier	Immersed Density, percent of theoretical	Area Density*, percent of theoretical
ASR&T	99.7	—
SSC	98.75	93.3
HUA	92.84	94.4
Trans-Tech	92.88	90.4
*Determined from SEM images		

The highest sintered density, 99.7 percent of theoretical density (ThD), was achieved in the tapes made with LaCrO_3 prepared by ASR&T. The materials supplied by SSC and HUA densified to greater than 94 percent of ThD. The density measured by the immersion-in-water technique for the HUA compares well with the density obtained from the polished surface (i.e., area density). This sample comparison does not hold as well for the SSC sample, perhaps indicating a significant error in the water immersion measurement. At 90 percent of ThD, the density of the Trans-Tech LaCrO_3 was the lowest of the powders analyzed. The lower degree of reactivity of this powder can be attributed to its large particle size. Analysis of the powder morphologies shown in Figure 7-29 suggests that this powder would densify the least of the four compared.

The SSC powder was selected for further study. An in-depth analysis of the powder was carried out on two lots of powder. The goal of the study was to determine what modifications of the powder surface area and morphology were necessary so that the powder could be used in the tape calendaring process. The powder was evaluated for surface area as a function of calcination time and temperature, and ball milling. Samples were further evaluated for densification and shrinkage at 1400°C.

Two lots of powder (030147 and 030201) of the same composition were prepared by SSC using the same preparation method. The as-received surface areas vary from 4.8 m^2/gm to 3.1 m^2/gm . These two lots were calcined in the same furnace following identical calcination schedules. Figure 7-30 shows the surface area as a function of calcination time.

Figure 7-30. Surface Area of Modified SSC LaCrO_3

B-22046

Tapes could not be fabricated with either of the as-received powders. Consequently, both lots had to be calcined to reduce the surface area to between 1 and 2.5 m^2/gm . Lot 030147 was calcined at 1000°C for 10 hr and the resulting surface area was 1.9 m^2/gm . A tape was easily fabricated with this material. Two samplings of Lot 030201 were calcined, one at 900°C for 5 hr, the second at 1000°C for 5 hr, and were then ball milled for 24 hr before being fabricated into tapes. The surface areas of these powders were 2.0 and 1.8 m^2/gm , respectively. Tapes were easily formed from these two batches. Figure 7-31 compares the powder morphology as a function of calcination and ball milling. The as-received powder, Figure 7-31(a), has soft, hollow spherical agglomerates of interconnected lanthanum chromite particles. After calcination at 1000°C (Figure 7-31(b)) the lanthanum chromite particle size increases; however, the spherical nature of the powder agglomerate remains. Ball milling can be used to break up the agglomerates as indicated in Figure 7-31(c).

Single-layer tapes of the two lots of powder were sintered under identical conditions and were evaluated for densification at 1400°C. Samples from Lot 030147 densified to 98.75 percent of ThD, while samples from Lot 030201 densified to only 93.8 percent of ThD, indicating that Lot 030147 is the more reactive. This was further verified in the X-ray diffraction patterns for the two lots. The peak corresponding to the phase CaCrO_4 is much larger in the spectra for Powder 030147, implying that more liquid phase is present during sintering, which will lead to greater densification in samples made from this lot of powder.

10μm

F-60110

Figure 7-31. $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Powder

The densities of three single-layer tapes fabricated with LaCrO₃ Lot 030201 were compared to determine the effect of calcination on densification. The as-received powder was calcined at 1000°C and 900°C for 5 hr and was then ball milled for 24 hr. These two samples were compared with samples of as-received material that was only ball milled for 24 hr and then made into a tape. The tapes made from these samples were sintered at 1400°C for 1 hr; the resulting linear shrinkages and densities are shown in Table 7-23.

TABLE 7-23 LINEAR SHRINKAGE AND DENSITY OF Ca, Co LaCrO ₃ SINTERED AT 1400°C FOR 1 HR				
Sample Preparation	Surface Area, m ² /gm	Shrinkage, Percent	Density, gm/cm ³	Theoretical Density, Percent
Ball mill 24hr*	3.5	19.4	6.12	94.4
Calcine 900°C/5hr Ball mill 24hr	2.0	18.2	6.10	94.2
Calcine 1000°C/5hr Ball mill 24hr	1.8	16.8	6.08	93.8
*Difficult to form tape				

It was observed that as the surface area (particle size) decreased, the linear shrinkage and sintered density decreased. This indicates that further calcination of the powder, additional to the manufacturer treatment, decreases the reactivity of the powder. Based on this analysis, the agglomerate structure needs to be broken down via a milling step, and the solids loading of the tapes may need to be modified to ease tape formation for higher surface area LaCrO₃ powders.

Figure 7-32 shows SEM micrographs of fracture surfaces of the sintered samples. As seen from the micrographs (Figure 7-32 A, D, G, and J), poor densification occurred in the samples sintered at 1300°C for 1 hr. The samples with a Cr:Co ratio of 8.6 (Figure 7-32 B and C) showed improved densification at higher sintering temperatures. On the other hand, when sintered at 1350° and 1400°C, the samples with a Cr:Co ratio of 9.0 and 9.2 (Figure 7-32 H, I, K, and L) showed nearly complete densification. From the above results, it appears that a sintering temperature greater than 1300°C is required to densify Ca,Co-doped LaCrO₃, and higher Cr:Co ratio improves the sinterability of the material. Higher Cr:Co ratio probably produces more chromium-containing liquid phases in the material during sintering, resulting in improved densification.

The effect of the La:Ca ratio was evaluated in samples made with powders of La:Ca ratio varying from 3.8 (0.96) to 4.2 (1.04); the A:B ratio is shown in parenthesis. Samples were sintered at 1350° and 1400°C for 1 hr in air and the density and

F-65889

Figure 7-32. Micrographs of Fracture Surfaces of $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_x\text{Co}_{1.0}\text{O}_3$ for Different Cr:Co Ratios at 1300°C, 1350°C, and 1400°C for 1 Hr ((A-C) Cr:Co = 8.6, (D-F) Cr:Co = 8.8, (G-I) Cr:Co = 9.0, and (J-L) Cr:Co = 9.2)

1300°C

1350°C

1400°C

F-65888

Figure 7-32. (Continued)

microstructure of the sintered samples were evaluated. The density of the samples is listed in Table 7-24.

TABLE 7-24			
DENSITY OF LANTHANUM CHROMITE SAMPLES FOR VARYING LA:CA RATIO			
La:Ca Ratio	A:B Ratio	Sintering Temperature, °C	
		1350	1400
3.8	0.96	92.0	92.6
4.0	1.00	91.5	93.2
4.1	1.02	*	*
4.2	1.04	93.7	97.9
*The accuracy of the density values obtained for the samples was suspected; measurements are being redone.			

Figure 7-33 shows SEM micrographs of fracture surfaces of samples with an La:Ca ratio of 3.8, 4.0, and 4.1, sintered at 1350°C and 1400°C. The micrographs of the samples with a La:Ca ratio of 4.2 are shown in Figure 7-32, H and I. Figure 7-33 A to F show relatively no inherent differences in the microstructure of the samples, thus no changes in densification with these compositions. A comparison of Figure 7-33 A to F with Figure 7-32 H and I shows a dramatic increase in grain size of the samples having the La:Ca ratio of 4.2 and higher density. It appears that increasing the La:Ca ratio to 4.2 increases the density and grain size significantly. The reason for these increases may be due to a larger amount of transient liquid phases formed at that composition, resulting in grain growth and improved densification.

7.3.3 Stoichiometric Effects

Two lots of LaCrO_3 powder provided by SSC, Inc. were evaluated. The new lots (Lots 0290 and 0291) had the lanthanum-deficient composition of $\text{La}_{0.78}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$. The standard composition (currently in use) is stoichiometric $\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (Lot 0260). The two lots of lanthanum-deficient chromite powder were also made by different synthesis processes. This study was to evaluate the effect of the synthesis method and composition on sintering, shrinkage, and microstructure of lanthanum chromite.

The chromite powders were made into tapes, and disc samples were fired at 1400°C for 1 hr in air. The sintered samples from Powder Lots 0290 and 0291 (lanthanum-deficient lanthanum chromite) had densities of 93.63 and 97.56 percent of theoretical density, respectively. Samples of Lot 0260 (stoichiometric lanthanum chromite) were sintered to 97.54 percent of theoretical density. The fracture surfaces of all three samples are shown in Figures 7-34(a) through 7-34(c). The microstructures,

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Figure 7-33. SEM Micrographs of $\text{La}_x\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ Sintered at 1350°C and 1400°C with (A-B) $x = 0.76$, (C-D) $x = 0.80$, and (E-F) $x = 0.82$

a. LOT 0290, La DEFICIENT

b. LOT 0291, La DEFICIENT

c. LOT 0260, STOICHIOMETRIC

F-64179

Figure 7-34. Fracture Surface of SSC Ca-, Co-doped LaCrO_3

shown in Figures 7-34(a) (Powder Lot 0290) and 7-34(b) (Powder Lot 0291), are comparable although the sintered samples using Powder Lot 0290 showed a higher degree of porosity than the samples using powder Lot 0291. It appears that the synthesis methods used in this case have little effect on the sintering characteristics and properties of the powder. A comparison of the sintered microstructures of Lots 0291 and 0260 (Figures 7-34(b) and 7-34(c) indicates that a 2 mole% deficiency in lanthanum also has little effect on sintering and microstructural development of lanthanum chromite.

SSC, Inc., a supplier of LaCrO_3 powders, carried out an analysis to determine the stoichiometry of Ca, Co-doped lanthanum chromite (lot 147) supplied to AlliedSignal. Their analysis indicated that the powder had a 10 percent excess of lanthanum, which displaced calcium and led to the formation of excess calcium chromate during sintering. Based on this analysis, a second lot of powder with 4 percent excess calcium was prepared.

Chromite powder with a composition of $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (A-site rich with 4 percent excess calcium) was received from SSC and fabricated into a tape. Samples were sintered at 1400°C and 1350°C for 1 hr. The samples sintered at 1400°C densified to 97.9 percent theoretical density (ThD), while those sintered at 1350°C densified to 97.7 percent ThD. Figure 7-35 shows SEM micrographs of two Ca,Co-doped lanthanum chromite compositions (stoichiometric and A-site rich) sintered at 1400°C for 1 hr. The composition of the material shown in Figure 7-35A is stoichiometric (A-site:B-site = 1) and the material has a density of 94 percent theoretical. Figure 7-35B is the SEM micrograph of a sample prepared with A-site rich material (A:B = 1.04) and sintered to 98.0 percent ThD. The A-site rich composition appeared to have more liquid phase during firing, resulting in higher densification.

Based on these results, a more detailed evaluation of Ca,Co-doped LaCrO_3 powders of various compositions was performed. The evaluation concentrated on the effects of varying Cr:Co and La:Ca ratios on the densification (and microstructure) of the double-doped material. The compositions evaluated were $\text{La}_{0.84}\text{Ca}_{0.2}\text{Cr}_{0.9\pm x}\text{Co}_{0.1}\text{O}_3$ (for varying Cr:Co ratios) and $\text{La}_{0.84\pm x}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$ (for varying La:Ca ratios).

The effect of the Cr:Co ratio was evaluated in samples made with Ca,Co-doped LaCrO_3 powders (supplied by SSC, Inc.) of Cr:Co ratio varying from 9.2 (1.02) to 8.6 (1.08); the A:B (La:Cr) ratio is shown in parenthesis. As-received powders were batched, rolled into tapes, and sintered at 1300°C , 1350°C , and 1400°C for 1 hr in air. Sintered samples were then characterized for density and microstructure. The density was measured using the buoyancy in water technique. The microstructure was examined by scanning electron microscopy. The results of the density measurements are listed in Table 7-25.

(a) $A/B = 1$

(b) $A/B = 1.04$

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Figure 7-35. Fracture Surfaces of Ca, Co-doped LaCrO_3 Sintered at 1400°C for 1 Hr

TABLE 7-25				
DENSITY OF LANTHANUM CHROMITE SAMPLES FOR VARYING CR:CO RATIO				
Cr:Co Ratio	A:B Ratio	Sintering Temperature, °C		
		1300	1350	1400
8.6	1.08	*	*	*
8.8	1.06	*	92.0	92.8
9.0	1.04	*	93.7	97.9
9.2	1.02	*	92.9	96.8
*Unable to accurately measure density due to La(OH) ₃ formation on surface of lanthanum chromite during density measurement.				

7.4 MICROCRACK CONTROL

7.4.1 Objective

The objective of this task was to improve fracture toughness of ZrO₂ electrolytes of MSOFC's by microstructural control through second phase additions.

7.4.2 Results

ZrO₂ electrolyte specimens with and without Super Z additions were evaluated. The specimens were 1-in.-dia. disks (~10 to 14 mils thick) of cubic ZrO₂ (identified as EH002-01 to 20), and its composites with 30-percent Super Z additions (EH005-01 to 21). These specimens were sintered in air at 1350°C for 1 hr. Evaluation of mechanical properties of dense ZrO₂ electrolyte specimens with and without 30 volume percent Super Z additions has been completed. The fracture toughness of cubic ZrO₂ electrolyte specimens increased from 2.1 to 3.8 MPa√m as a result of 30-percent Super Z additions. The corresponding increase in strength was 185 to 201 MPa. Weibull plots for failure probability (F) distribution of strength data for these specimens were constructed as shown in Figure 7-36. The Weibull modulus, m, was calculated from the slope of the lines in the ln-ln plot (Figure 7-36), which indicates that m was 4.71 and 2.65 for cubic ZrO₂ with and without Super Z additions. The small values of m suggest large scatter in the data. Further studies will continue on specimens containing various fractions of Super Z and/or other additions to cubic ZrO₂.

Figure 7-36. Weibull Failure Probability Distributions for Cubic ZrO_2 (Δ) and Cubic ZrO_2 + 30 Percent Super Z ($\circ$) Composite Specimens